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DETERGENCY OF CARBON BLACK

PART VI. THE STABILITY AND MECHANISM OF SETTLING OF CARBON BLACK DISPERSIONS IN ORGANIC LIQUIDS*

By F. H. Garner,† C. W. Nutt,† and M. F. Mohtadi †

Summary

Dispersions of carbon black (Micronex) in organic liquids and in solutions of detergent additives can be classified into three groups :—

(1) Rapidly settling dispersions in which, after a short induction period, a sharp liquid–dispersion interface is formed and the final sediment volume is very large.

(2) Dispersions which sediment very slowly indeed without the formation of an interface, and in which the final sediment volume is very small.

(3) Non-settling dispersions which exhibit no evidence of settling over periods of many months.

In dispersions of the first group, the volume occupied by the suspended carbon decreases exponentially with time; for a given system and time, this volume is independent of the size or shape of the containing vessel. A theory based on hindered aggregation under Brownian motion gives a satisfactory interpretation of the form of the settling. The energy barrier which hinders aggregation is related to the work involved in the displacement of interfacial liquid between aggregating particles. Such aggregation appears to give rise to a chain and scaffolding network of particles in the system. A mechanical picture of the sedimentation process has been postulated, and the formation and movement of the sharp interface have been explained in the light of gradual collapse of such a network. Further, it has been shown that the theory of scaffolding structures gives a better explanation of the large final sediment volume of carbon black dispersions than the theory of solvation. In group 3 the energy barrier precludes aggregation; group 2 is intermediate.

On the basis of the above theoretical considerations, a correlation has been found between the settling rate and the product of the density and surface tension of the dispersing liquid. This is similar to that previously observed experimentally for a range of organic liquids. The viscosity of non-settling dispersions is also discussed.

Introduction

Detergent additives, which are usually compounds of a complex nature, are added to lubricating oils to ensure the dispersion in the oil of carbonaceous materials resulting from the incomplete combustion of fuel and partial oxidation of the lubricating oil. In order to elucidate the mode of operation of these detergents, a study has been made of the properties of carbon black dispersions in a range of organic liquids and of hydrocarbon solutions of detergent additives.

Carbon dispersions were prepared with the aid of ultrasonic vibrations as described in a previous paper.[1] The carbon black (Micronex) sample was composed of granules formed, during manufacture, by the aggregation of primary particles having an average diameter of approximately 280 Å.‡

* MS received 13 March 1953.

† Department of Chemical Engineering, University of Birmingham.

‡ Based on nitrogen adsorption isotherms.

Electron-micrographs of a number of dispersions showed [2] that the large aggregates of carbon break down during dispersion with ultrasonics and that the extent of this deflocculation depends upon the detergent efficiency of the medium. Some re-aggregation takes place during the " drying " of the dispersion on the electron microscope slide, and the extent to which this occurs is also dependent on the detergent efficiency of the medium. For strongly detergent liquids, the electron-microscope shows mainly individual (or primary) particles, with some small aggregates, while, for weak detergents, only large aggregates are seen.

Dispersions prepared with 0·1 to 0·7 gm of Micronex in 25 ml of a liquid may be classified into three groups according to the behaviour on standing. The first group of dispersions shows a sharply defined interface between clear liquid and opaque dispersion while settling, and after a few days the level of this interface remains nearly constant. The second group requires several months to sediment, but in these dispersions the entire volume of liquid retains an opaque appearance throughout; the opacity, however, decreases with time, and sedimentation occurs. Finally, a third group of dispersions exhibits no evidence of sedimentation over periods of many months.

The first group of dispersions includes most of the systems which have been investigated. The height of the sharply defined interface between clear liquid and the opaque dispersion decreases exponentially with time, and from the settling curve thus derived the detergent properties of the liquid may be assessed. A characteristic of all these systems is the large final sediment volume of the dispersion, usually of the order of 8 to 12 ml. This is many times larger than the original volume occupied by the Micronex (in air). For dispersions in pure organic liquids and binary liquid mixtures, the settling curves may be correlated with the product of the density (ρ) and surface tension (γ) of the liquids [4]; the most powerful detergents have high values of $\rho\gamma$. It has also been noted that the more efficient detergent liquids usually have high dielectric constants.

For dispersions in toluene or heptane solutions of additives, the detergent properties can be correlated with the extent to which the additive is adsorbed on the carbon black.[2, 4] Additives which are not significantly adsorbed have negligible detergent properties, whilst strongly adsorbed additives are powerful detergents. The degree of adsorption increases to a maximum value as the additive concentration increases. Similarly, the detergent properties of solutions, as measured by the sedimentation curve, increase with concentration in a parallel manner.

For both pure liquids and solutions of detergents, the presence of a polar group (*e.g.*, NO_2; NH_2; Ca; and halogens) in the molecule gives rise to strongly detergent properties.

The second group of dispersions included certain commercial additives in dilute solution. Settling was observed to take place very slowly over a period of many months, without the formation of any sharp interface between clear liquid and dispersion. The entire liquid phase remained cloudy, but after a few weeks a powerful light source behind the settling vessel showed the presence of a layer of completely opaque sediment at the bottom of the tube. The volume occupied by this sediment increased with time, whilst the opacity of the liquid phase decreased correspondingly.

In contrast with the large final sediment volume observed in systems which settle by forming a clear liquid–dispersion interface, the volumes of these sediments closely approach the volume occupied by the dry carbon in air.

Of the third type of dispersion, no settling was observed over periods of several months with pure organic liquids with large values of $\wp\gamma$. Dispersions prepared in toluene solutions of the commercial additive E behaved in a similar way.

Electrokinetic phenomena similar to those which occur in aqueous systems are exhibited in Micronex dispersions very strongly.[5] This may be due in part to the high electrical resistivities of organic liquids, since all manifestations of the electrical double layer are inverse functions of the electrical conductivity of the medium. Thus the low conductivities of organic liquids enhance the effect of even small zeta potentials at the interface. Electrophoresis of the dispersed carbon particles has been demonstrated experimentally; and electric fields have been shown to modify the rate of settling and the final sediment volume of the dispersion. An externally applied electromotive force causes the sedimentation of carbon particles even in systems in which no settling takes place under gravity alone. Coagulation of the particles and their sedimentation to a very small final sediment volume can occur in mixtures of two dispersions in which the particles have adsorbed charges of opposite sign. In dispersions settling under gravity, sedimentation potentials have been detected, the potential gradients encountered being of the order of several hundred millivolts per centimetre. The electro-osmosis of the liquid phase in carbon dispersions has also been demonstrated.

In the present paper further experimental results are reported on the mechanism of the settling process and on the viscosity of dispersions. These results, together with those previously published,[1–5] are discussed in the light of existing theories of the behaviour of dispersions.

Any comprehensive theory of the structure and the mechanism of settling of carbon organosols must explain the following characteristic features :—

1. The viscosity behaviour of the dispersions.
2. The mechanism of settling of the dispersions, including :—

the kinetics of the sedimentation;
the formation of the sharp interface between the dispersion and the liquid;
the existence of an induction period prior to settling;
the influence of the liquid phase on the dispersion behaviour;
the electrokinetic properties; and
the large final sediment volume.

Viscosity of Non-settling Dispersions

Viscosities of dispersions containing up to 3 per cent by volume of Micronex in nitrobenzene, and in a toluene solution of commercial additive *E* were determined at 15° ± 0·1° C, using Ostwald viscometers Nos 3 and 4.

Fig 1 shows the relative viscosities of dispersions as a function of concentration, compared with the curve predicted by the Einstein equation :—

$$\frac{\eta_s}{\eta_d} = \eta_R = 1 + 2{\cdot}5C$$

where C is the solid concentration.

It will be seen that the relative viscosity of non-settling dispersions (as measured in capillary tube viscometers) deviates considerably from the value predicted by the Einstein equation when the volume concentration is in excess of 0·25 per cent. This limit is considerably smaller than that

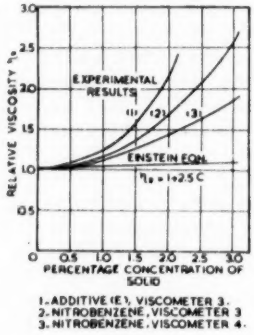

Fig 1

usually considered to be the limiting concentration for the application of this theoretical equation. Further, the magnitude of the deviation increases with decrease of diameter of the capillary in the viscometer.

The curves of Fig 1 are suggestive of the exponential type of equation

$$\ln \eta_R = f(C)$$

derived for high concentration of suspended solids by theoretical elaboration of the Einstein equation ; [16, 17] but the explanation of the variation with viscometer size is not readily apparent. Since the particles are of very small size as compared with the capillary diameters it is unlikely that wall effects are responsible for this difference. The electrical repulsive forces between the particles eliminate the possibility of formation of loose aggregates of the type considered in the theories of McDowell and Usher [13] and Goodeve.[18] Electro-kinetic phenomena cannot be excluded, although the Smoluchowski's equation [19] predicts a linear relation between η_R and C with a modified Einstein constant.

Mechanism of Settling of Dispersions

Effect of the Shape of the Settling Vessel

A dispersion containing 2 gm of Micronex, in 100 ml of toluene, was prepared in the manner previously described.[1-5] Settling curves were measured at 20° C for 25-ml samples of this dispersion in four cylindrical

vessels of different diameters. The internal diameters of the vessels, *A*, *B*, *C*, and *D*, were such that the initial heights of the dispersions were 35, 56, 93, and 280 mm respectively. Fig 2 shows a plot of the movement of the dispersion–liquid interface as a function of time.

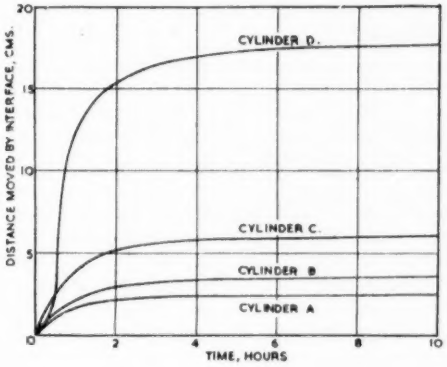

FIG 2

These curves show that the velocity of descent of the interface is a function of the initial height of the dispersion. The curve for vessel *D* (that in which the initial height was greatest) shows evidence of an induction period. It was noted that this induction period corresponded with the existence of a rather diffuse interface.

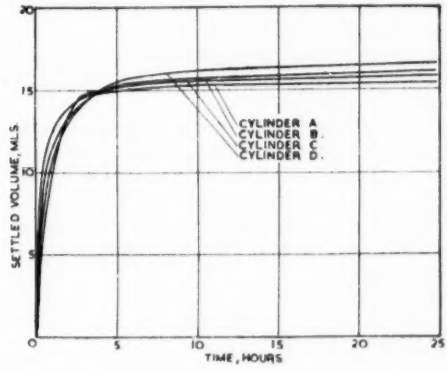

FIG 3

The same data are replotted in Fig 3 using "volume settled" * as ordinate. It is evident that the volume occupied by the dispersion at any instant is about the same, regardless of the physical shape of the

* The term "volume-settled" is used throughout to denote the volume of clear liquid above the opaque dispersion.

vessel and also of the rate of descent of the interface. There are some slight differences, particularly in the final sediment volume which decreases slightly as the initial height of the dispersion is increased.

Similar results were obtained for dispersions of 0·5 gm of Micronex in 25-ml samples of methyl *cyclo*hexane.

The Process of Aggregation

Conventional concepts of the settling of solid particles in a liquid involve the assumption that the motion of an individual particle is determined only by its size, shape, and density and is governed by Stokes' Law. Perturbations may be introduced due to the proximity of the vessel walls and ends, and adjacent particles. The effects of capillary electrical phenomena have also been noted.[6]

The present experiments on the effect of size and shape of the vessel clearly show, however, that the settling process for carbon dispersions in organic liquids is of an entirely different character. The initial velocity of descent of the clear liquid–dispersion interface is proportional to the height of dispersion below the interface. The volume of the dispersed phase decreases exponentially with time, and the rate is independent of the size and shape of the vessel and greater than that predicted by Stokes' Law. Thus, for toluene dispersions in tube *D*, the maximum velocity attained by the clear liquid–dispersion interface is of the order of 20 cm/hour; this corresponds to the terminal velocity predicted by Stokes' Law for an isolated spherical particle of graphite (density 2·25 gm/cm^3) with a diameter of 7000 Å, falling freely under gravity in toluene (density 0·864 gm/cm^3, viscosity 0·58 centipoises). The Micronex particle, however, is not spherical, its density is probably less than that of graphite, and the rate of fall of particles close together should be less than that for single particles. All these factors suggest that the diameter of the smallest particles must be greater than 7000 Å. Electron micrographs, however, show the presence of many particles with diameters considerably less than this limit (Fig 1 F of Part II [2]).

The exponential decrease with time of the volume occupied by the dispersion has previously been noted for other systems,[7] but the full implications have never been considered. It can be understood if the assumption is made that the rate of sedimentation is governed by the rate of aggregation of individual particles under the action of Brownian motion in the manner described below. This type of coagulation has been termed by P. Tuorila [8] " perikinetic " coagulation.

The observations show that aggregation, even in dilute dispersions, takes place at a rate which is fast compared with the settling rate of individual particles. This was observed from measurements of optical turbidity. Thus, toluene dispersions, prepared in the normal manner and diluted one hundredfold, show a considerable decrease of turbidity after 3 min, and large aggregates can then be seen in the system.

The Final Sediment Volume

A further point for discussion is the large final sediment volume formed from some dispersions. The two principal hypotheses which have been proposed are :—

(1) The theory of solvation.
(2) The theory of chain and scaffolding structures.

The solvation theory postulates the existence of a lyosphere of solvent molecules attached to each particle, and a considerable weight of evidence has been given in its support by Henniker [10] from many widely different experimental fields. Anisotropic forces at the solid–liquid interface orientate the solvent molecules into a quasi-crystalline structure, which may be described, by analogy with theories of liquid structure, as a cybotactic layer.[11] A layer of polar surface active molecules at the interface would enhance the phenomena.

The chain and scaffolding theory has also been discussed and considered by many investigators. The evidence rests largely on theoretical [11] and microscopic investigations [12–14] of the aggregation of dilute dispersions, which show that the formation of a linear chain of particles is more probable than a spherical aggregate. Electrical conductivity of carbon dispersions in organic media has sometimes been interpreted in terms of this theory, but such work has always neglected the importance of electrophoresis of the particles.[14, 15]

An estimate of the thickness of solvated layer required by the theory of solvation in order to explain the large final sediment volumes may be made in the following manner. The volume occupied by 0·5 gm of dry Micronex in air is of the order of 0·5 ml, whilst this amount of Micronex gives final sediment volumes of the order of 10 ml in most organic liquids. This twentyfold increase in volume requires that solvation increases the particle diameter 2·7-fold. Surface area measurements by gas adsorption suggest an average particle-diameter of 280 Å. Thus, the thickness of the solvated layer must be 240 Å, *i.e.*, of the order of 50 to 100 solvent molecules thick. The value of 280 Å for the particle diameter is, however, a minimum estimate since it neglects surface irregularities. Electron micrographs suggest particle diameters tenfold greater, necessitating an adsorbed layer thicker by a corresponding factor. The solvation theory therefore seems to be an unlikely explanation of the large final sediment volume.

Since the settling mechanism can be interpreted satisfactorily on the basis of the formation of a chain and scaffolding network of particles and aggregates enclosing liquid within the voids, it is more likely that this structure persists in the final sediment. This is supported by the evidence of Fig 3 which indicates that the final sediment volume is decreased as the hydrostatic pressure is increased.

With relatively stable dispersions such as in dilute solutions of strong detergents which do not exhibit a clear liquid–dispersion interface, the final sediment volume is very small (of the order of 0·5 ml). Here, the aggregates which settle out are relatively few in number, and no chain and scaffolding network can be built up; the final sediment volume is therefore about the same as that of the sum of the volumes of the individual aggregates.

Mechanism of the Sedimentation Process

A mechanical picture of the sedimentation process may be postulated as follows. Aggregation of the particles gives rise to a chain and scaffolding network of particles and aggregates, which extends throughout the entire

volume occupied by the dispersion, and which encloses other suspended particles in the voids of this framework. The electron-micrograph of Fig 1 F of Part II [2] shows part of such an aggregate chain from a very dilute toluene dispersion. Particles continuing to aggregate on to the network cause the network to collapse gradually through overloading at weak points in its structure. The settling of the interface is due to this gradual collapse of the network. The rate of collapse of the network is therefore controlled by the rate of adhesion of new particles to the network. The collapsing network gives rise to the sharp interface, since the probability of an individual particle in a void in the network escaping into the supernatant liquid is very small.

The rate of removal of individual particles by diffusion towards, and aggregation on, the lattice network may be estimated in the following manner. If $\bar{x}^2$ is the mean square distance of a particle from the lattice network, then the average time θ required for diffusion of a single particle to the network is :—

$$\theta = \bar{x}^2/kD \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is a constant depending on the geometry of the network * and D is the diffusion coefficient given by

$$D = RT/6\pi\eta_i Nr \quad . \quad . \quad . \quad . \quad (2)$$

where η_i is the viscosity of the liquid, r the radius of the particle, and N the Avogradro number.

At time θ, in V^D ml of dispersion containing n^D free particles per ml, the total number of collisions (Z) with the lattice per sec is given by

$$Z = V_\theta{}^D n_\theta{}^D kD/\bar{x}^2 \quad . \quad . \quad . \quad . \quad (3)$$

Now, the aggregation process involves passage over an energy barrier of magnitude E, so that the total number of collisions per sec which result in aggregation (Z') will be

$$Z' = V_\theta{}^D n_\theta{}^D (kD/\bar{x}^2) \exp(-E/RT) \quad . \quad . \quad (4)$$

$$= V_\theta{}^D n_\theta{}^D K \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $$K = (kD/\bar{x}^2) \exp(-E/RT). \quad . \quad . \quad . \quad (6)$$

The rate of change in the number of *free particles which remain trapped in voids in the dispersion* is therefore

$$d(V_\theta{}^D n_\theta{}^D)/d\theta = -V_\theta{}^D n_\theta{}^D K \quad . \quad . \quad . \quad . \quad (7)$$

and if it is assumed that $n^D{}_\theta$ and $\bar{x}^2$ remain constant during the process of sedimentation

$$d(V_\theta{}^D)/d\theta = -V_\theta{}^D K \quad . \quad . \quad . \quad . \quad (8)$$

Integrating,

$$\ln(V_\theta{}^D) = -K\theta + C \quad . \quad . \quad . \quad . \quad (9)$$

where the constant C may be determined from the initial condition at $\theta = 0$, $V_\theta{}^D = V_0 =$ the initial volume of dispersion.

* In the one-dimensional case G. Klein [3] shows that $k = 2$, and that for the diffusion of a particle at the centre of a sphere to the boundary $k = 6$.

Then,

$$\ln (V_\theta^D/V_0) = -K\theta \quad . \quad . \quad . \quad . \quad (10)$$

or

$$V_\theta^D = V_0 e^{-K\theta} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The rate of change of the number of *particles attached to the lattice* will be,

$$\frac{d(V_\theta^D n_\theta^D)}{d\theta} = V_\theta^D n_\theta^D K \quad . \quad . \quad . \quad . \quad (12)$$

and the rate of change of volume (V_θ^L) occupied by the lattice, excluding the voids, will be

$$\frac{dV_\theta^L}{d\theta} = \frac{d(V_\theta^D n_\theta^D)}{d\theta} \cdot \frac{1}{n_\theta^L} = \frac{V_\theta^D n_\theta^D}{n_\theta^L} \cdot K \quad . \quad . \quad (13)$$

where n_θ^L is the number of particles per ml in the lattice. If n_θ^L is also assumed to be constant during the sedimentation process, it follows from equation (13) (since $V_\theta^D n_\theta^D / n_\theta^L = V_\infty - V_\theta^L$) that

$$dV_\theta^L/d\theta = (V_\infty - V_\theta^L)K \quad . \quad . \quad . \quad (14)$$

or

$$\frac{d(V_\theta^L)}{(V_\infty - V_\theta^L)} = Kd\theta \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where V_∞ = volume occupied by the dispersion at infinite time.
Integration gives

$$-\ln (V_\infty - V_\theta^L) + C' = K\theta \quad . \quad . \quad . \quad (16)$$

where the constant C' may be evaluated at the condition $\theta = 0$, $V_\theta^L = 0$

$$C' = -\ln V_\infty \quad . \quad . \quad . \quad . \quad . \quad (17)$$

then

$$\ln\left(\frac{(V_\infty - V_\theta^L}{V_\infty}\right) = -K\theta \quad . \quad . \quad . \quad (18)$$

or

$$V_\theta^L = V_\infty (1 - e^{-K\theta}) \quad . \quad . \quad . \quad . \quad (19)$$

Then the total volume occupied by the dispersion (V_T) is given by the sum of equations (11) and (19)

$$V_T = V_\theta^D + V_\theta^L \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$V_T = V_0 e^{-K\theta} + V_\infty (1 - e^{-K\theta}) \quad . \quad . \quad . \quad (21)$$

or

$$V_T - V_\infty = (V_0 - V_\infty) e^{-K\theta} \quad . \quad . \quad . \quad (22)$$

or

$$\ln\left(\frac{V_T - V_\infty}{V_0 - V_\infty}\right) = -K\theta \quad . \quad . \quad . \quad (23)$$

where

$$K = (kD/\bar{x}^2) \exp(-E/RT) \quad . \quad . \quad . \quad (24)$$

Now, the energy barrier E will be equal to the work involved in displacing a mass of liquid from the region between the particle and aggregate against the force of surface tension. If the volume involved is the same for different liquids,

$$E = \chi\rho\gamma \quad . \quad . \quad . \quad . \quad . \quad (25)$$

when χ is some constant depending on the volume displaced and ρ and γ are the density and surface tension of the liquid respectively. Thus

$$K = (kD/\bar{x}^2) \exp(-\chi\rho\gamma/RT) \quad . \quad . \quad . \quad (26)$$

or

$$\ln K = \ln(kD/\bar{x}^2) - \chi\rho\gamma/RT \quad . \quad . \quad . \quad . \quad (27)$$

If the term $\ln(kD/\bar{x}^2)$ is small, then, for different liquids

$$\ln K \propto \rho\gamma \quad . \quad . \quad . \quad . \quad . \quad (28)$$

It has been shown that the settling curves may be represented in a satisfactory manner by equation (23) (Part IV [4]) and further (Fig 7, of Part IV [4]) that there is a linear relation between ln K and $(\rho\gamma)$ as predicted by equation (28) for dispersions in a wide range of organic media.

This experimental verification of the above equations gives strong support for the suggested mechanism of settling. Equations (27) and (28) are also consistent with the experimental observations that the viscosity of the liquid is of little importance in the phenomenon; viscosity is important only in the first term of equation (27) in so far as it affects the diffusion coefficient D.

The induction period (noted earlier in the section on effect of shape of the settling vessel), which occurred in conjunction with a somewhat diffuse interface, corresponds to the finite time required for the lattice to build up from individual particles and acquire rigidity, and to enmesh the individual particles. The induction period was less marked as the initial height of the dispersion is decreased, as would be expected, since the linear velocity of settling of the top of the scaffolding network will be slower in such cases.

Settling in solutions of some detergent additives takes place by the formation of a sharp interface, and the settling curves are in good agreement with equation (23). The $\rho\gamma$ criterion, equation (28), however, breaks down. This may be due to two factors. The value of ρ employed is that for the bulk liquid and not that for the material adsorbed at the interface. Further, the energy of the electric double layer contributes a large term to the value of γ, and the use of values of γ for the air–liquid interfaces is doubtful where surface active agents are present.

Conclusion

The formation, by hindered aggregation under Brownian motion, of a chain and scaffolding network, which extends throughout the system, provides a satisfactory explanation of the characteristic features of the large group of carbon dispersions in organic liquids which settle by the formation of a sharp interface. It provides a satisfactory explanation of the kinetics of the sedimentation process, the formation of the sharp interface, the induction period, and the influence of the liquid phase. It

shows how the electrical properties of the solid–liquid interface are related to the stability of the system, and it also gives an explanation of the very large final sediment volume exhibited by the systems.

The concepts provide explanations of the behaviour of the other two types of carbon dispersions, *i.e.*, the completely non-settling dispersions, and the systems which settle without the formation of a sharp interface.

In non-settling dispersions, the particles are of colloidal size, and are maintained in suspension by Brownian movement. In organic liquids with large values of $\rho\gamma$, the energy barrier to aggregation is so high that the translational energy of collisions by Brownian motion of the particles at normal temperatures is not sufficient to overcome the barrier and to form a stable aggregate. Thus, a completely stable suspension is formed. Application of an electric field can, however, impart sufficient kinetic energy by electrophoresis to overcome the barrier and cause aggregation.

In those dispersions which settle without the formation of a sharp interface, the settling process extends over several months. These dispersions are usually dilute solutions of strongly detergent additives, and they represent a transition between stable and the more rapidly settling dispersions. Brownian motion maintains the particles in suspension, but the energy barrier is of such a magnitude that aggregation proceeds at a finite, but exceedingly slow, rate. An aggregate just large enough to be incapable of being maintained in suspension by Brownian motion will be able therefore to settle to the bottom of the vessel, without increasing significantly in size. Thus, at any instant there is only a small concentration of small aggregates separating out, and the formation of a lattice network by the interaction of the aggregates is not possible.

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MOLECULAR DISTILLATION APPARATUS WITH GREAT SEPARATING POWER*

By W. G. Aldershoff, H. Booy,† S. L. Langedijk, G. Th. Philippi, and H. I. Waterman (Hon. Fellow)

Summary

An apparatus for molecular distillation with considerable separating power has been described. Nine stages of vaporization and condensation are provided in which the liquid phase is transferred from stage to stage by mechanical means. In this way, the separating power of the still is greatly increased compared with that of single-stage apparatus. A mixture of di-*n*-butyl-phthalate and di-*n*-butyl-azelate was employed for measuring the separating power under different reflux ratios and for comparing the separation with that obtained using a single-stage still.

An increase in reflux ratio from 3 : 1 to 7·5 : 1 gave greatly improved separation, the separation at 7·5 : 1 reflux ratio being very similar to that obtained under total reflux.

Introduction

Molecular distillation (short-path distillation in a very high vacuum) has become important as a method of separation for substances which are sensitive to high temperatures. In such cases, the usual methods of distillation cannot be used.

As is known,[1] the principle of molecular distillation is that a vaporizing surface of liquid is placed opposite, and a short distance away from, a condensing surface, the pressure between the two surfaces being kept very low (*e.g.*, < 1 μ Hg) so that distillation takes place at as low a temperature as possible and the thermal decomposition is reduced to a minimum. This low distillation temperature is one of the most important advantages which this method of distillation has over normal vacuum distillation.

One of the disadvantages is that the molecular distillation apparatus generally has low separating power because the distillation takes place in a single stage. During recent years several methods have, it is true, been published in which the separating power has been considerably improved; but construction of the apparatus is complicated.

These methods involve repeated distillation, a distillate being continually redistilled and the residue being fed back. The apparatus described here is based on this principle.

Principle

Fig 1 shows diagrammatically the streams of liquid and vapour in the apparatus, $C_1 - C_n$ being the condensing and $V_1 - V_n$ the vaporizing

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† The apparatus described here has already been published as part of H. Booy's Thesis, "De moleculaire destillatie als hulpmiddel bij het onderzoek van aardolieresiduen" ("Molecular distillation as an aid to the investigation of petroleum residues"), Delft, 1952.

surfaces. The liquid to be distilled is fed from tank A on to V_1, mixed with residue from surface V_2, and partially vaporized. The condensate on C_1 is fed on to surface V_2, mixed with residue from surface V_3, and again

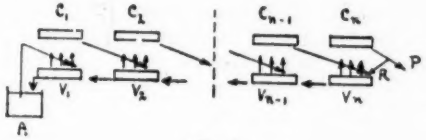

FIG 1

DIAGRAMMATIC REPRESENTATION OF THE PROCESS IN THE APPARATUS

partially vaporized. This process continues until the distillate reaches the last condensing surface C_n. Part (P) of the condensate on this surface is tapped off, the rest (R) being fed back as reflux. In this way, passing from C_1 to C_n, a progressive enrichment of the liquid in its most volatile components is obtained.

THE APPARATUS

The apparatus (Fig 2) is made of heat-resisting glass and chromium-plated brass. The heated surface is formed by tube F, in which is fitted

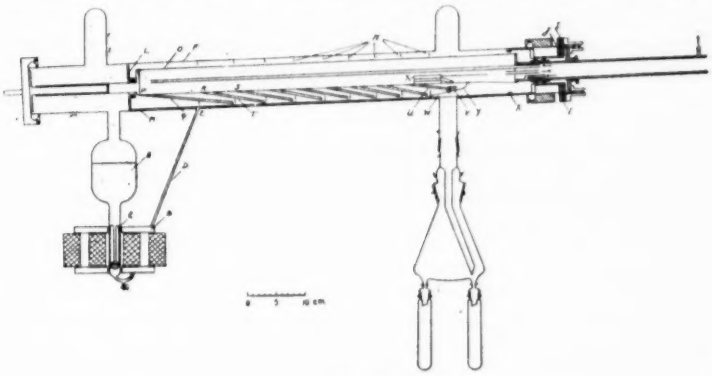

FIG 2

APPARATUS FOR MOLECULAR DISTILLATION WITH GREAT SEPARATING POWER

a cooled metal inner tube O, the latter being provided with ducts. The whole apparatus is set so that the tube slopes to one side and the ducts to the other. Between the cooled and the heated surfaces there is a stirrer, to spread the liquid in a thin film on the entire heated surface of tube F. This stirrer consists of a collar K and a plate L, linked by three rods M fitted with rings N to make them rigid.

Between K and L are three taut steel wires of 0·6 mm dia pressed against the surface of the tube F by means of small springs screwed on to the rings N, so that when the stirrer is rotated they drag across that surface and

spread the liquid. The stirrer is mounted on two ball bearings and is driven by the rotating permanent magnets I, which entrain the pieces of soft iron J attached to the stirrer.

The liquid to be distilled is transferred from storage tank A by an electromagnetic pump C and pipe D, to point E of tube F, where it is spread out into a film by the stirrer. Here the liquid is partially vaporized. The condensate forms on the cooled surface of the inner tube, O, between P and R, and runs off via the lowest point P of this tube, via the duct Q, to a point on the warm surface lying higher than E. Here the liquid is again spread out and distilled, and condenses on tube O between points R and S. The condensate returns to the heated surface via duct T. This process continues until the condensate reaches the duct U. From here it runs back as reflux past tap V and metal strip W, or, if the tap is turned by switching on an electromagnet X, it can be tapped off via strip Y.

The distilling surface is heated electrically by resistance wire wound round it, this winding being arranged so that the various distillation segments can be heated separately. During distillation, the temperature of these segments is usually increased regularly as the volatile components disappear from the mixture being distilled.

Distillations

A number of distillations were carried out with the apparatus described above in order to test the *separating power* qualitatively, to examine the effect of the *reflux ratio* on this power, and to determine the time required for the *establishment of a distillation equilibrium*.

Separating Power

In order to determine the superiority of this apparatus over the single-stage apparatus, a number of distillations were carried out with mixtures of di-*n*-butyl-phthalate and di-*n*-butylazelate as suggested by F. E. Williams,[2] who determined the relative volatilities at 1 mm Hg. At this pressure the boiling points of the phthalate and azelate are 150° and 155° C respectively. The advantage of using these two components is the great difference in refractive index, so that by measuring the refractive index of the distillate fractions their composition can be determined rapidly and accurately.

A quantity of 200 ml of a mixture of about 80 mol % azelate and 20 mol % phthalate was distilled for 1 hour with total reflux, the residual air pressure in the apparatus being less than 0·1 μ Hg at 68° C, which was the same for all segments. The mixture was then distilled for a further hour, the distillate being tapped off in a constant reflux ratio (*i.e.*, quantity of reflux/quantity tapped off) of 3. This reflux ratio was obtained by periodically setting the reflux tap V (Fig 2) to total reflux and tapping off by means of a time switch. The switching cycle was always one minute, so that to obtain a reflux ratio of 3 the distillate was tapped off for 15 seconds per minute.

After an hour the distillation was interrupted by breaking the vacuum. The temperature during this distillation was so low (68° C) that this could be done without risk of oxidation.

A sufficient amount of liquid now remained suspended from each of the ducts of the condensing body for it to be possible, by measuring the refractive index, to determine the composition of the condensate on each of the condensing surfaces at the moment the distillation was interrupted.

Table I shows what the composition of the condensate was.

TABLE I

	Mol % of phthalate
Composition of residue in retort A . . .	19·5
Composition on condensing surface No. 1 . .	28·7
" " " " No. 2 . .	33·2
" " " " No. 3 . .	42·7
" " " " No. 4 . .	52·9
" " " " No. 5 . .	58·5
" " " " No. 6 . .	59·2
" " " " No. 7 . .	61·6
" " " " No. 8 . .	65·5
" " " " No. 9 . .	71·2

It is clear that progressively there is a considerable enrichment of the liquid in its most volatile component. As no data are known concerning the relative volatilities of the two components at the low pressure and temperature employed, Table I gives only a qualitative picture of the separating power, and a figure for plate efficiency cannot be deduced.

The apparatus can, however, be compared with a single-stage type. With a falling-film apparatus, for example, a mixture of dibutyl phthalate and dibutyl azelate with 59 mol % of phthalate yields a distillate with 70 mol % of phthalate.

It can, therefore, be said : to obtain a product with 70 mol % one must start, in the case of the falling-film apparatus, with a product with 59 mol % of phthalate, whereas with the new apparatus, it is sufficient to start with a product with only 20 mol % of phthalate, provided a reflux ratio of 3 is used.

THE EFFECT OF THE REFLUX RATIO ON THE SEPARATING POWER

To obtain good separation with distillation apparatus, it is generally necessary to work with a small tap-off and a large reflux ; with small reflux ratios, the separating power falls off considerably. An investigation was made to determine the effect of the reflux ratio with this apparatus, and separation with a given reflux compared with that obtained by working with total reflux.

The tests were carried out so that distillation first took place for an hour at a given reflux ratio. After distillation had been stopped, by breaking the vacuum, a determination was made of the composition of the liquids on the various surfaces. Distillation was then resumed for a further hour with the remaining liquid and with total reflux. The composition of the liquid on the various surfaces was then again determined.

As the amount of residue was very large in relation to the amount of liquid on the surfaces, the composition of the residue was the same in both cases.

The results are summarized in Table II.

TABLE II

Reflux ratio	3	∞
Mol % phthalate in residue	19·5	19·5
,, ,, on surface 1 . . .	28·7	33·2
,, ,, ,, ,, 2 . . .	33·2	52·3
,, ,, ,, ,, 3 . . .	42·7	66·1
,, ,, ,, ,, 4 . . .	52·9	74·4
,, ,, ,, ,, 5 . . .	58·5	78·5
,, ,, ,, ,, 6 . . .	59·2	79·2
,, ,, ,, ,, 7 . . .	61·6	80·7
,, ,, ,, ,, 8 . . .	65·5	81·4
,, ,, ,, ,, 9 . . .	71·2	80·0

Reflux ratio	$7\frac{1}{2}$	∞
Mol % phthalate in residue	33·2	33·2
,, ,, on surface 1 . . .	44·0	40·5
,, ,, ,, ,, 2 . . .	58·5	58·5
,, ,, ,, ,, 3 . . .	69·8	69·1
,, ,, ,, ,, 4 . . .	75·5	76·2
,, ,, ,, ,, 5 . . .	79·3	78·1
,, ,, ,, ,, 6 . . .	80·0	79·0
,, ,, ,, ,, 7 . . .	81·1	79·9
,, ,, ,, ,, 8 . . .	81·0	79·8
,, ,, ,, ,, 9 . . .	79·3	78·1

It is clear from Tables I and II that with a reflux ratio of 3 the separating power is exploited only very inadequately, since on the first four surfaces the same separation with total reflux is obtained as from nine surfaces with a reflux ratio of 3. A reflux ratio of $7\frac{1}{2}$ is sufficient to obtain the best possible separation. With this reflux ratio, the rate of tapping off is still sufficiently large to enable the distillation to be carried out within a reasonable period of time.

THE TIME REQUIRED FOR THE ESTABLISHMENT OF A DISTILLATION EQUILIBRIUM

With distillation columns operating at atmospheric or moderately lowered pressures, and in particular with those which have a high separating power, distillation must first take place for considerable time with total reflux to enable an equilibrium to be established in the column, before tapping off can be started. This is also to be expected with the apparatus described above.

A number of tests was made to determine the time for an equilibrium to become established, and hence when tapping off can begin. This time was roughly determined by distilling dibutyl phthalate, to which aminoazobenzene had been added, distillation taking place with total reflux.

The colour of the liquid at the drainage end of the apparatus gradually became a less intense yellow, the colouring matter being less volatile than the dibutyl phthalate; as an equilibrium was reached the less volatile colouring matter was displaced by the more volatile phthalate. After an hour's distilling, no further change of colour was to be observed.

The time required to reach an equilibrium was determined more precisely by distilling a mixture of dibutyl phthalate and dibutyl azelate. A quantity of 200 grams of the mixture with 77·2 mol % of phthalate was distilled. After the distillate had reached the drainage end of the apparatus, a few drops were tapped off. This was repeated 10, 65, 135, 165, and 230 minutes later.

The composition of the drops is indicated in Table III.

TABLE III

Time, minutes	Mol % phthalate
0	85·7
10	89·2
65	91·7
135	92·0
165	92·3
230	91·8

Table III shows that after an hour the equilibrium became sufficiently established to allow tapping off of the distillate to start.

DISTILLATION OF PETROLEUM PRODUCTS

To illustrate the application to distillates of crude oil residues, the results of four examples of predistillation in the falling film still (325° C, pressure $< 1\ \mu$ of mercury) are given in Table IV.

TABLE IV

Distillation No.	Quantity of raw material, g	Quantity of distillate, g	Quantity of distillate re-distilled, g
XVIII	369·2	254·7	249·8
XXI	207·0	155·6	152·8
XXII	214·9	160·9	158·1
XXXV	268·8	246·8	242·6

The results of redistillation in the apparatus with great separating power are given in Table V (reflux 7·5; 53 seconds per minute total reflux; 7 seconds per minute tapping off).

The losses of distillations XVIII, XXI, XXII, and XXXV were respectively 5·1, 0·8, 4·5, and 3·1 grams.

CONCLUSION

An apparatus for molecular distillation with considerable separating power was tested with a binary mixture, the results indicating that the separating power was considerably better than with the known single-stage apparatus.

TABLE V

Fraction	Wt, g	n_D^{70}	$d_{70°C}$	Mol wt	% Carbon naphthenic	% Carbon aromatic	% Carbon paraffinic	No. of aromatic rings	No. of naphthene rings
XVIII, 1	12·8	1·5195	0·9432	347	48·2	22·8	29·0	0·96	3·04
XVIII, 2	44·9	1·5148	0·9351	365	46·7	20·5	32·8	0·93	3·09
XVIII, 3	46·4	1·5178	0·9388	387	44·6	21·5	33·9	1·04	3·12
XVIII, 4	44·9	1·5178	0·9317	432	33·6	23·3	43·1	1·24	2·84
XVIII, 5	46·1	1·5192	0·9316	510	28·0	23·5	48·5	1·54	2·82
XVIII, 6	49·6	1·5317	0·9509	742	23·2	26·0	50·8	2·40	3·70
XXI, 1	8·2	1·4858	0·8755	334	31·5	17·1	51·4	0·69	1·80
XXI, 2	22·2	1·4820	0·8685	351	29·2	15·8	55·0	0·65	1·75
XXI, 3	20·0	1·4812	0·8695	372	30·4	14·0	55·6	0·61	1·95
XXI, 4	21·1	1·4854	0·8768	379	30·8	15·3	53·9	0·70	1·98
XXI, 5	21·7	1·4854	0·8736	408	25·9	15·4	58·7	0·76	1·83
XXI, 6	21·2	1·4827	0·8654	437	19·8	15·8	64·4	0·83	1·52
XXI, 7	37·6	1·5106	0·9103	512	19·1	23·6	57·3	1·53	1·98
XXII, 1	10·9	1·5010	0·8995	325	32·7	22·5	44·8	0·89	1·90
XXII, 2	22·5	1·4932	0·8871	356	30·1	19·1	50·8	0·82	1·88
XXII, 3	22·3	1·4913	0·8850	374	29·9	17·5	52·6	0·80	1·95
XXII, 4	21·2	1·4922	0·8835	390	26·1	18·6	55·3	0·88	1·82
XXII, 5	16·9	1·4914	0·8789	410	21·0	19·1	59·9	0·96	1·57
XXII, 6	22·4	1·4938	0·8809	414	19·1	20·7	60·2	1·06	1·44
XXII, 7	37·4	1·5263	0·9337	550	15·9	29·3	54·8	2·07	2·07
XXXV, 1	15·8	1·4984	0·8888	331	24·5	24·1	51·4	0·99	1·44
XXXV, 2	29·1	1·4873	0·8668	350	17·0	22·0	61·0	0·94	1·06
XXXV, 3	34·0	1·4810	0·8588	357	19·2	18·6	62·2	0·80	1·14
XXXV, 4	36·7	1·4773	0·8522	373	17·3	17·1	65·6	0·78	1·08
XXXV, 5	37·8	1·4728	0·8406	402	11·0	16·8	72·2	0·82	0·63
XXXV, 6	45·1	1·4751	0·8484	449	12·9	15·0	72·1	0·80	0·97
XXXV, 7	41·0	1·5180	0·9165	627	9·8	27·2	63·0	2·19	1·56

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INVESTIGATION OF THE SULPHUR COMPOUNDS PRESENT IN MIDDLE DISTILLATE SO_2-EXTRACTS*

By R. Emmott †

Summary

A reliable analytical method was devised for the types of sulphur compounds present in middle distillates, and carefully tested for its accuracy and limitations. The SO_2-extracts from Texas, Iraq, and Kuwait kerosines were analysed. All contained large amounts of aliphatic and cyclic sulphides, these accounting for over one-third of the total sulphur values. The Kuwait extract contained only traces of free sulphur, hydrogen sulphide, mercaptans, and disulphides, whilst thiophenes were absent. "Residual" sulphur compounds represented one-half the total sulphur. The Texas extract, however, contained small but appreciable amounts of mercaptans, disulphides, and thiophenes, whilst the proportion of "residual" sulphur was much less. Analyses of the Iraq extract gave values intermediate between the other two samples.

The mercaptans were isolated from the Texas oil by means of their cadmium salts, and freed from hydrocarbons by a repeat extraction process.

The Kuwait reactive sulphides were obtained free from hydrocarbons in a single-stage process by means of their water-soluble mercuric acetate complexes. This procedure was tested, and gave very satisfactory and reliable results. Fractionation of the mixed thioethers, followed by further separation of the fractions through their mercuric chloride addition compounds, did not lead to the isolation of any pure components. These Kuwait thioethers appear to contain many constituents in appreciable amounts, but few compounds are present in large proportions. Refractive index values indicate that the compounds present consist almost entirely of alkyl-substituted cyclic sulphides. 3-*n*-Butylpentamethylene sulphide was synthesized, and possessed very similar physical and chemical properties to the lower thioether fractions. Preparation of cyclic sulphides containing seven- and higher-membered rings demonstrated that only the five- and six-membered types are likely to be present in petroleum distillates.

Part of the Kuwait unreactive sulphur compounds was isolated from the treated SO_2-extract by means of aluminium chloride, and almost freed from aromatic hydrocarbons by a repeat extraction process. The reliability of this method was tested and found satisfactory. Physical constants indicate that these "residual" sulphur compounds consist of bicyclic sulphides; they most probably represent fused ring-systems with the hydrocarbon ring joined in the α-position to the sulphur atom.

Discussion

An investigation of the chemical and physical properties of the sulphur types in middle distillates was undertaken as a preliminary step to the isolation and characterization of individual compounds. During recent years, comprehensive studies have been made of the sulphur-containing bodies present in light distillates. However, little research has been carried out on the higher fractions, owing to the complexity of the problem and the requirement for a new technique. No individual sulphur compounds

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† Petrocarbon Ltd.

have been characterized from the kerosine fraction. Furthermore, very few sulphur derivatives in this boiling range have been synthesized; hence, the chemical and physical properties of the majority are unknown. Work on this aspect is being carried out under API Project 48B.

A complete review of the sulphur compounds identified in petroleum was compiled by Haines *et al.*[1] A number of the lower molecular weight mercaptans, disulphides, thiophenes, and sulphides have been isolated from the gasoline fraction, generally from industrial extracts enriched in sulphur compounds, such as mercaptans from " solutizer " extracts and sulphides from sulphuric acid sludges. According to Birch and Norris,[2] branch-chain thiols predominate. Naphthenic thiols and thioethers appear to be absent in petroleum products; the presence of aliphatic and cyclic sulphides has been substantiated, and, of the latter class, tetramethylene and pentamethylene sulphides together with their methyl derivatives have been isolated.[3, 4] Friedmann and Rodriguez [5] give some interesting details of the cyclic sulphides in a kerosine fraction, whilst Fidler, Lowry, and Haresnape [6] isolated and identified a number of aliphatic and cyclic sulphides by means of adsorption on silica gel. The thioethers were, in general, finally purified through their mercuric chloride addition compounds. More recently, adsorption technique using activated alumina has been reported by API Project 48A; many of the lower aliphatic and cyclic sulphides were identified by their infra-red spectra. The use of fractionation and selective adsorption for separation of sulphur compounds from middle distillates had proved much less satisfactory, and new methods of approach were required.

In the present work, it appeared advisable to employ industrial extracts enriched in sulphur compounds, and the readily available SO_2-extracts were chosen, as the sulphur compounds originally present are probably unchanged by the refining process. The first requirement was a reliable analytical method for the sulphur groups. A satisfactory procedure was devised from those already recorded,[7–9] and was thoroughly tested for its accuracy and limitations. For the latter purpose, several sulphur compounds in the kerosine boiling-range were synthesized. The main improvement in technique was the separate removal and estimation of thiophenes by means of basic mercuric sulphate. This reagent proved very effective, and did not react with aromatic sulphides; mercuric nitrate does not differentiate between the two groups. Spielmann and Schotz [10] employed basic mercuric sulphate in coal-tar analyses. For the estimation of mercaptans, silver nitrate could be replaced by cadmium acetate with a sodium acetate buffer. Mercurous nitrate monohydrate appeared to be quite effective for estimation of higher molecular weight sulphides in oils, contrary to the observations of Borgstrom and McIntire.[11] Sulphur group analyses of SO_2-extracts from Kuwait, Iraq, and Texas middle distillates were carried out. In each extract, most of the sulphur content was accounted for by " reactive " sulphides, representing aliphatic and cyclic thioethers, and by " residual " sulphur compounds, which were not affected by the reagents employed. Some aromatic sulphides appear to be present. Only the Texas oil contained appreciable, though small, amounts of mercaptans, disulphides, and thiophenes, together with considerably less " residual " sulphur.

Mercaptans from Texas Middle Distillate SO_2-extract

The mercaptans were isolated from the Texas oil by means of their cadmium salts: $2RSH + Cd(Ac)_2 \longrightarrow (RS)_2Cd + 2HAc$. Treatment of the extract with aqueous cadmium acetate, buffered by sodium acetate, gave a gelatinous precipitate of the cadmium mercaptides, containing much occluded oil. The mercaptans were regenerated by dilute hydrochloric acid in the presence of light petroleum, and purified by a repeat extraction process, employing light petroleum to lower continually the amount of oil occluded in the precipitated mercaptide. This process gave a 40 per cent recovery of the mercaptans, which contained 15·6 per cent S. However, the quantity obtained was too small for further investigations. Strickland recorded [12] the isolation of mercaptans from kerosine by means of methanolic sodium hydroxide.

Most interest centred around the Kuwait extract, which was selected for further investigation. The original sample contained 1·40 per cent S, which on standing decreased to a limiting value of 1·38 per cent S. Treatment of the oil with sodium bicarbonate solution immediately lowered the sulphur content to the latter figure; it appears probable that the original sample still contained a little sulphur dioxide. Analysis indicated 0·6 per cent S as " reactive " organic sulphides, and 0·8 per cent S as " residual " sulphur compounds, all the other sulphur types being present only in traces. The problem of isolating the Kuwait " reactive " thioethers was thoroughly studied, and this included the testing of many reagents. Some concentration of the sulphides could be achieved by means of adsorption on silica gel, but the process was unsatisfactory owing to the highly aromatic nature of the extract. The difference in adsorptivity of the aromatic hydrocarbons and sulphides in this range appeared to be very small. As is well known, the sulphur atom in organic sulphides forms a co-ordinate link with suitable electrophilic reagents, the chief representatives of this type being the hydrogen ion from strong acids and the metal atom in other Friedel–Crafts catalysts. Most of these reagents also form addition complexes with aromatic hydrocarbons, but mercury salts are exceptions. However, mercuric chloride was unsuitable as an extractor, as the complexes formed were fairly soluble in the aromatic oil. Owing to the large diameter of the polar sulphate radical, basic mercuric sulphate gave an addition complex which was oil-insoluble. Treatment of the Kuwait SO_2-extract with this reagent completely removed all the reactive sulphides, the addition compound forming as a flocculent precipitate.

Far more promising results were obtained using mercuric acetate. This reagent proved to be an ideal extractor for thioethers from oils, as the mercuric acetate addition compounds are quite water-soluble. The remarkable solubility of these complexes was first reported [13] in 1926, but has only recently been appreciated. Birch and McAllan,[14] simultaneously with the present author, have developed the use of this reagent, and the two procedures differ only in minor details. Treatment of the Kuwait oil with aqueous mercuric acetate removed all the reactive thioethers as water-soluble complexes. However, in the case of these higher molecular weight sulphides, it was found advantageous to employ aqueous acetic acid in order to increase the extraction rate. The thioethers were

best regenerated from the addition complex by sodium sulphide, followed by steam distillation; the use of hydrochloric acid gave a somewhat lower recovery. The method was tested by employing a solution of *n*-dibutyl sulphide in kerosine; an almost pure sample of the thioether was obtained in 80 per cent recovery. In similar tests with synthetic mixtures, Birch and McAllan report failure to extract high molecular weight dialkyl sulphides. However, in the present work, dicapryl sulphide was easily extracted from a kerosine solution by mercuric acetate in aqueous acetic acid. Diphenyl sulphide was unaffected by this reagent, whilst phenylethyl sulphide was only partially, and very slowly, extracted from hydrocarbon solutions.

The regenerated thioethers appear to be entirely free from hydrocarbon impurities. Friedmann and Rodriguez [5] employed 60 per cent aqueous perchloric acid for removal of hydrocarbons from thioethers, but this reagent was without effect on the Kuwait sulphides, the refractive index being unchanged after treatment.

Reactive Sulphides from Kuwait SO_2*-extract*

The reactive thioethers isolated from a large amount of the Kuwait SO_2-extract were fractionally distilled at reduced pressure through an efficient column. No thermal decomposition of the sulphides was noted.[15] The sulphides up to an equivalent boiling point of 250° C were distilled directly, and these represented 60 per cent of the total charge; the remainder were fractionated after addition of a suitable chaser. A total of eighty, approximately equal, fractions were collected. The refractive index composition graph for the lower fractions shows "plateaux," which might represent partial separation into individual constituents or small groups of compounds. The corresponding graph for the higher fractions gives an almost smooth curve, containing a deep hollow around b.p. equivalent 260° to 270°; no further work has been carried out on this portion. Further purification of the lower boiling cuts by fractional crystallization of their mercuric chloride addition compounds failed to indicate the isolation of any pure components, although the original "plateaux" persisted in the new refractive index composition graphs. Hence, these Kuwait thioethers contain many constituents in appreciable amounts, and no compounds are predominantly present.

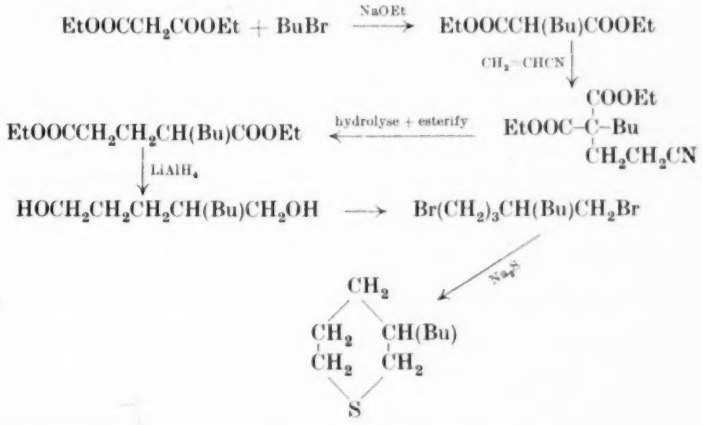
Nature of Kuwait Reactive Thioethers

(1) These substances must be saturated organic sulphides, as shown by the method of extraction and their unreactivity towards bromine–water. Their refractive indices (1·48 to 1·50) agree with the expected values for alkyl-substituted cyclic sulphides, and are much higher than those recorded (1·45 to 1·46) for aliphatic thioethers in this boiling range. Naphthenic sulphides have never been reported in petroleum fractions: from data available they would also possess somewhat lower refractive indices.[16] Hence, the indications are that the compounds present consist almost entirely of alkyl-substituted cyclic sulphides; small amounts of aliphatic sulphides and bicyclic compounds may also be present. Analyses of several selected fractions fully substantiate this conclusion; fraction b.p. equivalent to 170° at atmospheric pressure exactly corresponds to $C_8H_{16}S$, whilst

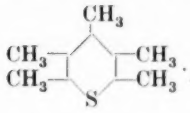
fraction b.p. equivalent to 224° exactly represents $C_{11}H_{22}S$. The lower-boiling Kuwait thioethers, b.p. 180° to 250°, range from $C_8H_{16}S$ to $C_{13}H_{26}S$.

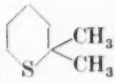
(2) The solubilities of the mercuric chloride addition compounds in alcohol are intermediate between those of the aliphatic thioether mercuric chlorides and the very insoluble complexes formed by the unsubstituted cyclic sulphides. There is a close connexion between stability and solubility, owing to dissociation of the complexes in warm solvents. Cyclic sulphides form more stable addition compounds than the aliphatic thioethers, and this phenomenon might be expected, as the restricted vibrations in the cyclic compound favour electron-availability at the sulphur atom. Alkyl-substituted cyclic sulphides should possess intermediate properties.

(3) β-*n*-Butylpentamethylene sulphide, $C_9H_{18}S$, b.p. 218°, was synthesized for testing :



This compound possessed very similar physical and chemical properties to the corresponding Kuwait thioether fraction. However, the refractive index of the thioether fraction is somewhat lower. Also, this fraction, b.p. equivalent 218°, corresponds approximately to $C_{11}H_{22}S$. These differences might possibly be explained by the presence in the thioether fraction of cyclic sulphides containing many small alkyl substituents, *e.g.*,



(4) Cyclic sulphides containing a tertiary carbon atom  are unlikely to be present. Aliphatic tertiary sulphides are decomposed by mercuric salts [14] :

$$t\text{-}C_4H_9SC_2H_5 + HgCl_2 \longrightarrow t\text{-}C_4H_9Cl + C_2H_5S\cdot HgCl$$

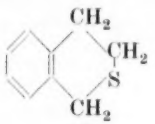
(5) Syntheses of cyclic sulphides containing seven- and higher-membered rings were carried out, to ascertain the probability of these types existing in natural oils. Results indicate that only five- and six-membered cyclic sulphides are likely to be present in a petroleum product. Hexamethylene sulphide was obtained in 30 per cent yield; decamethylene sulphide could not be prepared by a ring-closure synthesis. Cyclic thioethers containing three- and four-membered rings are easily formed in good yield, but these are surprisingly absent in petroleum fractions.

Nature of " Residual " Sulphur Compounds

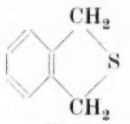
All the middle distillate SO_2-extracts contained residual sulphur compounds which were not affected by the analytical reagents. The Kuwait oil, after treatment, contained 0·75 to 0·8 per cent S as unreactive sulphur-containing bodies of unknown type, and the problem of isolating these was studied. The adsorbents, silica gel and alumina, had no effect; warm mercuric acetate solution appeared to react with some of these compounds. The only type of reagent to produce a decided lowering in the sulphur content of the oil were the most powerful Friedel–Crafts catalysts. Aluminium chloride proved the most promising, and removed half the " residual " sulphur from the Kuwait oil. Some aromatic hydrocarbons also formed addition products during the process. A concentrate of the " unreactive " sulphur compounds was regenerated, with about 40 per cent loss due to polymerization, and the Kuwait " unreactive " sulphur compounds were purified to a limiting sulphur value of 13·2 per cent by a repeat extraction process. The final product probably still contained traces of aromatic hydrocarbons; its high refractive index of 1·5300 is in the range of bicyclic compounds.

The aluminium chloride extraction method was tested, using a solution of *n*-dibutyl sulphide in kerosine, and extraction was slow and incomplete. The pure thioether was recovered from the addition complex; no isomerization or degradation of the sulphide occurred under the extraction conditions.

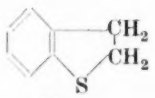
Birch and McAllan [14] investigated the effect of mercuric acetate on a few bicyclic sulphides. *iso*Thiochroman I and xylylene sulphide II reacted readily, whilst dihydrothionaphthen III was only very slowly and incompletely removed from petroleum :—



I.



II.



III.

Substitution in the α-position to the sulphur atom appears to have lowered the co-ordinating ability of the compound. Substances of types I and II may hence occur to a small extent in the Kuwait " reactive " thioether fractions. Indications are that the Kuwait " residual " sulphur compounds most probably consist of bicyclic sulphides, with the hydrocarbon ring joining in the α-position to the sulphur atom.

Experimental

Properties of Extracts

Origin	Iraq	Kuwait	Texas
Specific gravity	0·880	0·8875	0·9132
Flash point, ° F (P.M.)	144	148	146
Pour point, ° F	−60	−60	—
Aromatics, per cent, vol	72	74·5	—
Distillation :			
I.B.P., ° C	174	176	171
Per cent recovered :			
180° C	3	3·5	2·0
190° C	16·5	15	8·0
200° C	32·5	30·5	18·5
210° C	46	47	30·0
220° C	59	60	43·0
230° C	68	69	53·0
240° C	76·5	76·5	66·0
250° C	85·5	85	77·0
260° C	94	92·5	86·0
270° C	97·5	97	92·0
280° C	—	—	95·5
290° C	—	—	97·0
300° C	—	—	98·0
F.B.P., ° C	273	274·5	305
Copper strip corrosion	No change		

Analytical Procedure for Sulphur Group in Middle Distillates

(1) The total sulphur content of the sample was determined, using the new ASTM conditions (lamp-sulphur), the sample being diluted with pure kerosine if necessary. SO_2-extracts gave satisfactory burning properties when diluted with two parts of sulphur-free kerosine. The percentage of sulphur was similarly determined at each stage, the difference from the preceding value representing the sulphur content due to the class of sulphur compounds removed.

(2) Free sulphur was removed by metallic mercury, according to the directions of U.O.P. A.119–140.

(3) Hydrogen sulphide was removed by acidified cadmium chloride solution (U.O.P. A.119–140).

(4) *Mercaptans.* A sample (20 ml) was shaken for 40 min with 5 per cent aqueous cadmium acetate (50 ml) containing sodium acetate (3 g). After filtering, the oil was separated, and the extraction repeated. Finally, the oil was thoroughly washed with water, and again filtered.

Alternatively, the silver nitrate method of Ball,[8] employing a 40-min extraction time, gave satisfactory results.

Method IP 104/45T was employed to estimate very low mercaptan content. The accuracy of this procedure was not determined.

(5) *Disulphides.* These were reduced to mercaptans by zinc and acetic acid according to U.O.P. A.119–140, and the mercaptans estimated by process (4).

(6) *Open-chain and cyclic sulphides.* These were removed by vigorously shaking the sample with an equal weight of mercurous nitrate monohydrate, agitating for two periods of 30 to 40 min each. The sample was filtered

from the sulphide complex, washed with sodium carbonate solution, and dried by filtration.

This reagent had no effect on thiophenes or aromatic sulphides. Disulphides, if present, reacted to some extent.

(7) *Thiophenes.* These were removed by shaking the sample (20 ml) with basic mercuric sulphate solution (100 ml) for 40 min, filtering by suction and separating. The recovered oil was water-washed and dried by filtration.

This reagent was tested only with a mono-substituted thiophene. Under the above conditions, it had no effect on aromatic sulphides.

(8) *Aromatic sulphides.* These were removed by shaking the sample with an equal weight of mercuric nitrate monohydrate for 30 to 40 min. The mixture was then treated as in (6).

Preparation of Reagents

Sulphur-free kerosine. Commercial kerosine was shaken with one-third its volume of concentrated sulphuric acid. This process was repeated twice, and the remaining oil thoroughly washed with water, separated, and dried by filtration. The pure kerosine had a sulphur content of 0·000 to 0·003 per cent.

Mercurous nitrate monohydrate. Powdered, commercial mercurous nitrate dihydrate was allowed to remain in an evacuated desiccator over sulphuric acid until the required loss in weight had occurred (several days).

Basic mercuric sulphate solution. Yellow mercuric oxide (5 g) was dissolved in concentrated sulphuric acid (20 ml) and water (100 ml).

Efficiency of the Analytical Procedure

Compound added to pure kerosine	Reagent for removal	Initial % S	Final % S	% removal
Mercaptan :				
Ethyl mercaptan	Cadmium acetate	0·52	0·00	100
2-Octyl mercaptan	Cadmium acetate + NaAc	0·50	(*a*) 0·07	96
			(*b*) 0·02	
2-Octyl mercaptan	Alcoholic Na plumbite	0·07	0·05	30
n-Octadecyl mercaptan $C_{18}H_{37}SH$	Cadmium acetate + NaAc	0·12	0·01	92
Disulphide :				
Diethyl disulphide	Zn + CH_3COOH reduction, followed by $CdAc_2$ + NaAc	0·33	0·01	97
Sulphide :				
n-Dibutyl sulphide	Cadmium acetate + NaAc	0·13	0·13	Nil
	$HgNO_3 \cdot H_2O$	0·135	0·02	85
		1·14	(*a*) 0·045	99
			(*b*) 0·01	
Di-*sec*-butyl sulphide	$HgNO_3 \cdot H_2O$	1·00	(*a*) 0·03	98
			(*b*) 0·015	
Di-*sec*-octyl sulphide $C_{16}H_{34}S$	$HgNO_3 \cdot H_2O$	0·33	(*b*) 0·02	94
Pentamethylene sulphide	$HgNO_3 \cdot H_2O$	0·135	(*a*) 0·045	99
			(*b*) 0·01	
		0·90	(*a*) 0·48	50
			(*b*) 0·09	90

Compound added to pure kerosine	Reagent for removal	Initial % S	Final % S	% removal
Thiophene :				
Thiophene	$HgNO_3 \cdot H_2O$	0·33	0·33	Nil
	Basic mercuric sulphate	0·40	0·00	100
3-Methylthiophene	Basic mercuric sulphate	0·31	0·00	100
Aromatic sulphide :				
Phenyl ethyl sulphide	$HgNO_3 \cdot H_2O$	0·45	(*a*) 0·38	15
	Basic mercuric sulphate	0·58	0·48	16
Diphenyl sulphide	Mercuric nitrate	0·30	(*a*) 0·07	100
	$Hg(NO_4)_2H_2O$		(*b*) 0·00	
	Basic mercuric sulphate	0·30	0·29	Nil

(*a*) = once treated, (*b*) = twice treated.

Most of the compounds tested were in the kerosine boiling range, and they include a mercaptan, $C_{18}H_{37}SH$, and a sulphide, $C_{16}H_{34}S$, with boiling points around the upper limit of 300° C.

The analysis does not differentiate between open-chain and cyclic sulphides. Actual analyses of middle distillates always show a " residual sulphur " value, representing unreactive sulphur compounds not affected by the reagents used.

Colour Tests for Sulphur Groups in Kerosine

Mercaptans. The method of Mapstone [22] was checked, using 2-octyl mercaptan; it was more satisfactory than the " doctor " test for the presence of higher molecular weight mercaptans in kerosine.

The sample (5 ml) was shaken for 20 sec with 2*N*-NaOH (2 ml) and 1 per cent aqueous sodium nitroprusside (1 ml). The formation of a reddish-purple colour indicates the presence of mercaptans. The sodium hydroxide cannot be replaced by sodium carbonate.

Thiophenes. A small crystal of isatin was dissolved in 85 per cent sulphuric acid (5 ml), the sample (5 ml) added, and the mixture shaken for 5 sec. Development of a greenish-blue tinge in the acid layer indicates the presence of thiophenes. The bluish colour can be detected before serious darkening occurs.

Analysis of SO_2-extracts

Compound type	Iraq, % S content	Kuwait, % S content	Texas, % S content
Original extract	1·52 decreases to 1·42	1·40 decreases to 1·38	1·34 decreases to 1·17
Free sulphur	Trace	Trace	Trace
Hydrogen sulphide	Nil	Trace	Nil
Mercaptans	0·019	0·002	0·040
Disulphides	0·041	0·003	0·061
Aliphatic and cyclic sulphides	0·56	0·56	0·53
	0·59	0·60	0·55
Thiophenes	0·05	Nil	0·13
	0·08		0·11
Aromatic sulphides	0·24	0·12	0·22
Residual sulphur	0·48	0·71	0·18
Total	1·42	1·41	1·16

The decreases noted in the original sulphur contents of the extracts occurred after the oil had stood open to the air for several hours, the latter figures representing the final constant values. A similar decrease in sulphur content was rapidly obtained by shaking the sample with dilute sodium bicarbonate solution.

Separation of Sulphur Compounds from Extracts

Mercaptans from Texas Extract

Formation of cadmium mercaptides. The Texas extract (2 litres) was shaken for 3 hr with a solution of crystalline cadmium acetate (30 g) and sodium acetate (6 g) in water (300 ml). Most of the supernatant oil was decanted and reserved for a second treatment. A fresh sample of extract (2 litres) and a further amount of cadmium acetate (2 g) were added, and the process repeated. A volume of 22 litres of the extract was treated, the total cadmium mercaptides filtered off, and the oil retreated in a similar manner. The second small precipitate of mercaptides was added to the main batch. The treated oil contained no further mercaptans.

Regeneration and purification of mercaptans. The crude cadmium mercaptides contained much occluded oil. A mercaptan concentrate was regenerated by shaking the cadmium salts with hydrochloric acid (100 ml conc HCl + 100 ml water) in the presence of light petroleum (200 ml). Reprecipitation of the mercaptides from the petroleum solution by cadmium acetate (30 g) and sodium acetate (7 g) in water (300 ml) gave a much cleaner product. This process was repeated three times, the final cadmium mercaptides being obtained as a colourless crystalline substance.

The Texas mercaptans were regenerated by acid in the presence of light petroleum. Removal of the solvent from the dried extract gave 13 g mercaptans.

The " pure " Texas mercaptans, analysed for 15·6 per cent S as the original SO_2-extract, contained 0·04 per cent mercaptan S, representing a 40 per cent recovery of the thiols.

Aliphatic and Cyclic Sulphides from Kuwait Extract

Extraction. The Kuwait oil, sulphur content 1·42 per cent (1500 ml), was shaken for 30 hr with mercuric acetate solution (80 g mercuric oxide dissolved in 200 ml acetic acid and 130 ml water). Most of the supernatent oil was decanted, and the remaining liquor filtered. The acetic acid layer was separated, and twice extracted with light petroleum (40 ml each time).

The total Kuwait extract was then shaken with sulphuric acid (50 ml conc sulphuric acid and 50 ml water) for 12 hr. The sulphuric acid layer was similarly separated and extracted with light petroleum.

The treated Kuwait extract, after washing with water, had a sulphur content of 0·75 per cent (see p. 703).

During the initial extraction, a small amount of colourless crystalline precipitate was formed. This probably represents addition compounds of mercuric acetate with unsaturated substances.

Regeneration of sulphides. Ice (250 g) was added to the mixed acetic and sulphuric acid liquors, and a solution of crystalline sodium sulphide

(90 g) in water (200 ml) added below the surface of the mixed acid, with good stirring throughout. The precipitated mercuric sulphide carried almost all the thioethers. The precipitate was filtered off, and distilled in steam. The distillate gave 35 g mixed Kuwait sulphides; extraction of the acid filtrate yielded only further traces of thioethers.

TABLE I

Fraction	Wt, g	Total, g	n_{20}^{D}	B.p.	B.p. (760 mm), °C
A	3·30	3·30	1·4772	71·8–74·8	176
B	4·84	8·14	1·4775	73·8–77·2	179
C	4·71	12·85	1·4783	80·5	183·5
D	5·14	17·99	1·4786	83·5	186
E	4·53	22·52	1·4792	86·0	192·5
F	4·55	27·07	1·4794	88·8	195
G	4·39	31·46	1·4800	91·3	198
H	4·61	36·07	1·4804	93·5	202
I	4·19	40·26	1·4808	95·5	205
J	5·75	46·01	1·4812	97·5	207
K	4·75	50·76	1·4819	99·2	209·5
L	3·96	54·72	1·4820	100·4	211·5
M	3·88	58·60	1·4825	101·8	213
N	4·33	62·93	1·4829	102·8	215
O	4·19	67·12	1·4850	103·8	216
P	4·00	71·12	1·4829	104·9	217
Q	3·96	75·08	1·4839	105·2	218·5
R	5·28	80·36	1·4845	107·4	219
S	3·43	83·79	1·4850	109·4	222
T	3·04	86·83	1·4851	110·8	224
U	2·96	89·79	1·4858	112·0	225·5
V	5·83	95·62	1·4865	113·0	227
W	4·98	100·60	1·4872	114·0	228
X	4·02	104·62	1·4881	115·0	229·5
Y	4·12	108·74	1·4885	116·4	230·5
Z	5·56	114·30	1·4888	117·0	232·5
A′	4·42	118·72	1·4890	117·8	233
B′	4·16	122·88	1·4912	118·4	234
C′	4·81	127·69	1·4917	119·5	235
D′	5·71	133·40	1·4924	120·0	236
E′	3·15	136·55	1·4933	121·0	237·5
F′	3·98	140·53	1·4940	121·5	238·5
G′	5·06	145·59	1·4944	122·6	239·5
H′	4·54	150·13	1·4948	124·0	240·5
I′	5·56	155·69	1·4952	124·8	242
J′	6·61	162·30	1·4960	125·3	243
K′	5·87	168·17	1·4964	110·8	244
L′	4·31	172·48	1·4969	112·8	246
M′	6·75	179·23	1·4972	114·0	250
Trap	1·5	180·7	1·4030	—	—
Residue	178	359	1·5053	—	—

These Kuwait thioethers, after removal of any hydrogen sulphide, contained 16·4 per cent S, corresponding to an " average " sulphide between C_{11} and C_{12}. Recovery of thioethers was 75 per cent.

Fractional distillation of sulphides. The reactive sulphides obtained from 14 litres of Kuwait SO_2-extract amounted to 385 g. Properties: d_{20}, 0·94; n_D^{20}, 1·4960; per cent S, 16·4.

These Kuwait thioethers were fractionally distilled through a column packed with $\frac{1}{16}$-inch stainless steel helices. Initial distillation was at 20

mm pressure; from fraction K1, distillation was at 10 mm pressure. The higher-boiling portion of the charge required a separate distillation with addition of a chaser, owing to the column hold-up.

Conditions : Column 55 T.P. at 760 mm (n-C_7 — Me *cyclo*-C_8); boil-up rate 750 ml/hr; reflux ratio 7 : 1; fractions approx every 5 ml; charge 385 g; loss of product, 20 g (5 per cent of charge).

Higher-boiling fractions. These were distilled through the same column at 5 mm pressure after addition of a chaser.

Conditions : charge 176·5 g; n_{20}^{D} 1·5053 chaser; technical white oil topped to equivalent of 300° C, n_{20}^{D} 1·4738; boil-up rate 750 ml/hr; reflux ratio 4 : 1; fractions approx every 5 ml.

Further Separation of the Lower-boiling Thioethers (Table I)

The refractive index-composition graph for the lower-boiling fractions (Table I, Fig 1) shows indefinite " plateaux " which might represent partial

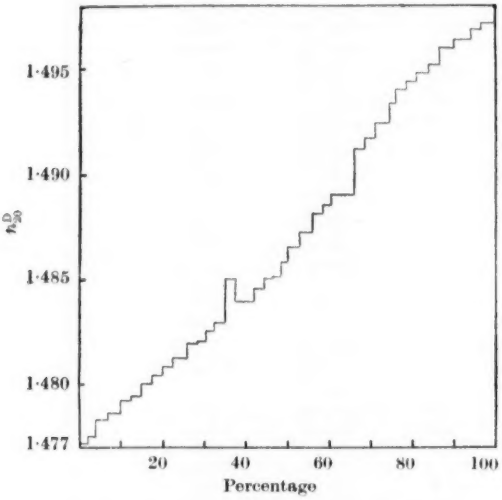


FIG 1

FRACTIONATION OF KUWAIT LOWER SULPHIDES

separation into individual constituents or small groups of compounds. The fractions were further separated through their mercuric chloride complexes.

Procedure. The mercuric chloride derivative of each of the fractions was prepared in alcohol (20 ml), using sufficient mercuric chloride to form theoretically the dimercuric chloride addition compound. Fractions M′ to A′ were assumed to represent C_{11} sulphides, Z to L C_{10} sulphides, and K to A C_9 sulphides. The addition complexes were soluble in warm alcohol; on cooling, they quickly separated as viscous semi-solids. The solutions were cooled slowly to 4°, the mother liquor decanted, and the thioether

regenerated by steam distillation in the presence of sodium sulphide. The thioethers were then shaken with sodium carbonate solution. The sulphides remaining in the mother liquors were similarly recovered, and the small amount from alcohol mother liquor of M′ added to the next lower fraction L′ before purification. This procedure was repeated throughout. The carry-through from the mother liquors was about constant, amounting

TABLE II

Fraction	Wt, g	Total, g	% Distilled	n_{20}^{D}	B.p.	B.p. (760 mm), ° C
(1)	4·7	4·7	2·66	1·4898	95	245
(2)	5·55	10·25	5·67	1·4959	96·2	247
(3)	4·65	14·9	8·45	1·4971	97·0	249
(4)	4·3	19·2	10·9	1·4977	98·2	—
(5)	4·4	23·6	13·4	1·4983	99·0	—
(6)	4·7	28·3	16·05	1·4990	99·3	250
(7)	4·3	32·6	18·5	1·4995	99·9	251
(8)	4·5	37·1	21·0	1·5003	100·5	—
(9)	4·6	41·7	23·6	1·5012	101·5	—
(10)	4·6	46·3	26·3	1·5020	102·0	254
(11)	4·7	51·0	28·9	1·5028	103·5	—
(12)	4·5	55·5	31·5	1·5034	103·7	—
(13)	4·6	60·1	34·1	1·5039	104·2	257
(14)	4·5	64·6	36·6	1·5041	105·0	—
(15)	4·7	69·3	39·3	1·5047	105·9	260
(16)	4·6	73·9	41·9	1·5049	106·5	—
(17)	4·6	78·5	44·5	1·5050	106·7	—
(18)	4·7	83·2	47·2	1·5052	107·2	—
(19)	4·5	87·7	49·7	1·5050	108·2	262
(20)	4·6	92·3	52·3	1·5043	109·8	—
(21)	5·0	97·3	55·2	1·5030	110·2	265
(22)	4·5	101·8	57·7	1·5037	110·8	—
(23)	4·6	106·4	60·4	1·5034	111·7	267
(24)	4·7	111·1	63·0	1·5034	112·7	—
(25)	8·2	119·3	67·5	1·5037	113·2	—
(26)	4·6	123·9	70·2	1·5038	113·5	—
(27)	4·9	128·8	73·1	1·5042	114·5	271
(28)	4·5	133·3	75·6	1·5044	115·5	—
(29)	4·9	138·2	78·3	1·5051	117·0	—
(30)	4·7	142·9	81·0	1·5038	119·5	278
(31)	4·7	147·6	83·7	1·5046	120·8	—
(32)	4·7	152·3	86·4	1·5043	122·0	282
(33)	4·5	156·8	88·9	1·5036	123·5	—
(34)	4·6	161·4	91·6	1·5021	125·5	286
(35)	5·0	166·4	94·3	1·5000	127·5	—
(36)	4·3	170·7	96·8	1·4977	128·0	289
(37)	3·8	174·5	99·0	1·4935	130·0	292
(38)	7·2	181·7	100 +	1·4880	132·0	295

The fractions from (30) onwards appear to be azeotropes with the white oil.

to 0·4 g. Treatment of the fractions was attended by a 16 per cent loss of thioethers.

Second purification. The above procedure was repeated, employing 1·5 mol mercuric chloride per mol sulphide. Here the carry-through from the mother liquors amounted to a constant value of 1·1 to 1·2 g thioether; 0·3 g of the carry-through was taken into account for purposes of calculation for the amount of mercuric chloride required.

The refractive index composition graphs (Figs 2 and 3) of the fractions

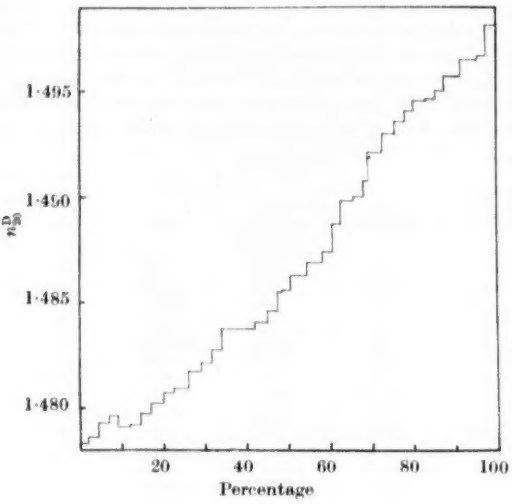


FIG 2

PURIFICATION OF KUWAIT LOWER SULPHIDES

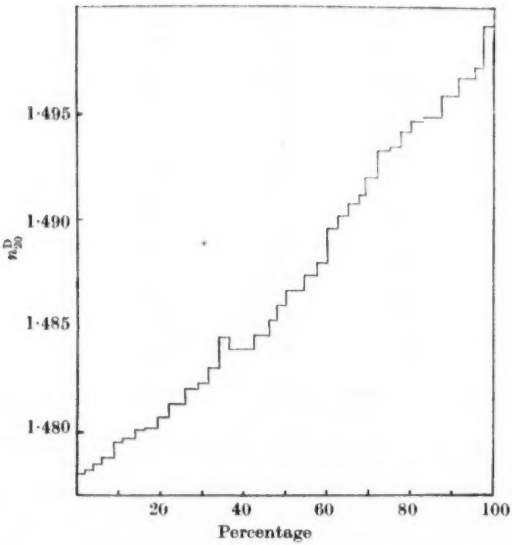


FIG 3

PURIFICATION OF KUWAIT LOWER SULPHIDES

from these two purifications retained the "plateaux" of the original Fig 1, but failed to indicate any improved separation of the constituent thioethers.

Efficiency and Accuracy of Mercuric Acetate Extraction Process

The method was tested by the use of a primary sulphide in kerosine. *n*-Dibutyl sulphide, b.p. 182° (10 g), was added to sulphur-free kerosine (500 ml), and extracted by the mercuric acetate process; 8·4 g of pure *n*-dibutyl sulphide, b.p. 182°, n_{20}^{D} 1·4529, were recovered, representing 80 to 85 per cent recovery for normal aliphatic sulphides. This value is higher than was obtained in extraction of the Kuwait thioethers. The treated kerosine mother liquor was sulphur-free.

Analysis. The recovered *n*-dibutyl sulphide was analysed (lamp sulphur). (Found 21·4 per cent S; $C_8H_{18}S$ requires 21·9 per cent S.)

A similar result was obtained on employing di-*sec*-butyl sulphide in kerosine solution.

Analysis of Several Lower-boiling Kuwait Sulphide Fractions and Comparison with Cyclic Sulphides CnH_2nS

Sulphide fractions were taken after second purification.

Fraction	B.p. (760 mm), ° C	Analysis	Cyclic sulphide	Requires
A	176	C 67·2% H 11·1% S 22·2%	$C_9H_{18}S$	C 66·7% H 11·1% S 22·2%
J	207	C 69·5% H 11·2% S 19·6%	$C_{10}H_{20}S$	C 69·8% H 11·6% S 18·6%
T	224	C 71·1% H 11·4% S 17·6%	$C_{11}H_{22}S$	C 70·9% H 11·8% S 17·3%
D′	236	C 72·8% H 11·3% S 16·4%	$C_{12}H_{24}S$	C 72·0% H 12·0% S 16·0%
M′	250	C 71·6% H 11·1% S 16·6%	$C_{12}H_{24}S$	C 72·0% H 12·0% S 16·0%

Isolation of Kuwait Residual Sulphur Compounds by means of Aluminium Chloride

The Kuwait SO_2-extract, after removal of the reactive thioethers, contained 0·74 per cent S. This treated extract (500 ml) was shaken with excess anhydrous aluminium chloride (40 g) during 16 hr. The unreactive sulphides formed an addition compound, which separated as a deep red oil. After standing for several hours, the supernatant layer was decanted, and the addition complex scrubbed twice with light petroleum (100 ml total). The unreactive thioethers were regenerated

by addition of ice. Steam distillation gave 35 g unreactive sulphur compound concentrate, sulphur content 6·2 per cent. This concentrate contains some aromatic hydrocarbons, which also give complexes with the aluminium chloride.

The recovered Kuwait oil, after washing with sodium carbonate solution, gave a sulphur value of 0·36 per cent. Loss of unreactive sulphides due to polymerization was 10 per cent. A total of 140 g Kuwait unreactive

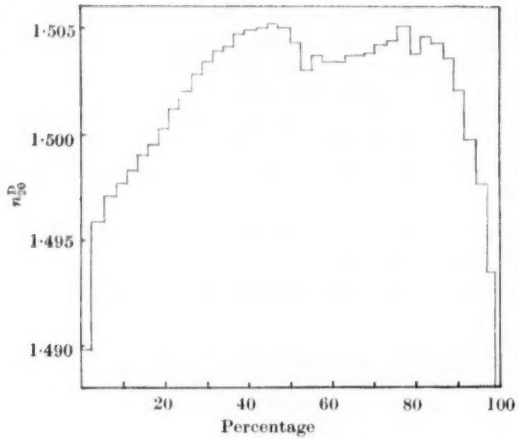


FIG 4

FRACTIONATION OF KUWAIT HIGHER SULPHIDES

sulphide concentrate, containing 4·55 per cent S, was obtained from 3 litres of Kuwait extract.

Purification. The unreactive sulphides were obtained almost free from aromatic hydrocarbons by a repeat extraction process (Table III), utilizing the fact that these sulphur compounds form more stable complexes with aluminium chloride than do the corresponding aromatic hydrocarbons. In each stage, the concentrate was diluted with light petroleum before extraction. The sulphides were regenerated as described above. The ligroin mother liquors were shaken with sodium carbonate solution, and most of the petroleum was removed by distillation, the residual oils containing some unextracted sulphur compounds.

TABLE III

Concentrate	G	% S	Light petroleum diluent, ml	$AlCl_3$, g	Product	Residual oil		% Loss polymer
						G	% S	
I	140	4·55	250	30	II	144	1·92	5
II	33	10·0	200	15	III	46·7	2·20	25
III	12·1	12·5	50	7	IV	4·5	5·8	40
IV	6·2	13·1	25	4	V	1·0	12·8	40
V	3·35	13·2	—	—	—	—	—	—

At stage V the process has reached the limit of purification. This was checked by examining the residual oil from stage IV, after careful removal of all the light petroleum. The following values were obtained :

	% S	n_{20}^{D}
Kuwait extract . . .	0·74	1·5040
Concentrate IV . . .	13·1	1·5296
Residual oil IV . . .	12·8	1·5288
Concentrate V . . .	13·2	1·5300

The final Kuwait unreactive sulphur compounds at stage V probably still contain a small amount of aromatic hydrocarbons, as the sulphur content is a little lower than expected. The refractive index is in the range of bicyclic compounds.

Efficiency and Accuracy of Aluminium Chloride Extraction Process

The method was tested for the extraction of *n*-dibutyl sulphide from kerosine. *n*-Dibutyl sulphide (5 g) in sulphur-free kerosine (50 ml) was shaken for 20 hr with anhydrous aluminium chloride (5 g). The addition compound slowly separated as an almost colourless oil. After scrubbing with light petroleum, the *n*-dibutyl sulphide (1·0 g, n_{20}^{D} 1·4552) was recovered from the complex by addition of ice, followed by steam distillation. No polymerization of the thioether was noted. The kerosine mother liquors (39 g) had a sulphur content of 1·77 per cent, corresponding to 3·2 g of unextracted *n*-dibutyl sulphide.

The recovered sulphide was purified through the mercuric chloride addition compound. Regeneration gave 0·5 g *n*-dibutyl sulphide, b.p. 182°, n_{20}^{D} 1·4529; pure *n*-dibutyl sulphide has a recorded b.p. 182°, and n_{20}^{D} 1·4528. The extraction of *n*-dibutyl sulphide by aluminium chloride was very slow and incomplete. However, no isomerization or degradation of the thioether occurred under the conditions employed.

Preparation of the Sulphur Compounds used in the Investigation

2-*Octyl mercaptan*. Capryl mercaptan was prepared from capryl alcohol, thiourea, and hydrogen bromide, followed by alkaline hydrolysis of the thiouronium salt, according to the directions of Frank and Smith.[17] The reaction product was fractionally distilled, and the crude 2-octyl mercaptan, b.p. 185·5° to 186·5°, further purified through its cadmium salt. The mercaptan was shaken with an excess of 10 per cent aqueous cadmium acetate containing sodium acetate buffer. The precipitated cadmium salt was filtered, washed with ligroin, and decomposed with dilute hydrochloric acid in the presence of light petroleum. The dried extract on fractionation gave a 32 per cent yield of 2-octyl mercaptan, b.p. 186° at 760 mm, n_{20}^{D} 1·4480, in agreement with values recorded in the literature.

n-*Octadecyl mercaptan*. Octadecyl alcohol (40 g), potassium bromide (3 g), and conc sulphuric acid (10 ml) were mixed and heated under reflux for 10 hr. The mixture was diluted with water, the bromide separated, shaken with conc sulphuric acid, then rewashed with water. The crude

octadecyl bromide, m.p. 20° to 21° C, amounted to 29 g. It was used without further purification. Octadecyl bromide (29 g), thiourea (9 g), and water (35 ml) were mixed, and heated under reflux for 5 hr; the thiouronium salt was hydrolysed by refluxing with sodium hydroxide (30 g) in water (60 ml) for 5 hr. The crude mercaptan solidified after acidification and cooling. Two crystallizations from acetone containing charcoal gave pure *n*-octadecyl mercaptan, m.p. 30° C, yield 10 g. This compound is not recorded in the literature. (Found 10·9 per cent S; $C_{18}H_{39}SH$ requires 11·2 per cent S.)

Di-2 octyl sulphide. Capryl alcohol (40 g), hydrobromic acid (48 per cent wt/vol (100 g)), potassium bromide (4 g), and conc sulphuric acid (18 ml) were mixed and heated under reflux for 5 hr. After dilution with water (100 ml), the capryl bromide was separated and purified by shaking with conc sulphuric acid, followed by rewashing with potassium carbonate solution. Distillation of the dried product gave 35 g capryl bromide, b.p. 189° C at 750 mm.

A mixture of capryl bromide (27 g) and crystalline sodium sulphide (23 g) in water (23 ml) and alcohol (30 ml) was heated under reflux for 18 hr. The product was diluted with water and ether extracted. Fractional distillation of the dried extract gave 9 g dicapryl sulphide, b.p. 120° C at 3 mm; n_{20}^{D} 1·46065. There was a yield of 40 per cent from the bromide. This appears to be a new compound. (Found 12·2 per cent S; $C_{16}H_{34}S$ requires 12·4 per cent S.)

Di-sec-butyl sulphide. Di-sec-butyl sulphide, b.p. 165°, n_{20}^{D} 1·45096, was prepared from *sec*-butyl alcohol by an analogous procedure. Reaction time 3 hr; yield 50 per cent from the bromide.

Di-tert-butyl sulphide. Conc sulphuric acid (11 ml) was added during 3 min with good mixing to *tert*-butyl mercaptan (19 g) and *tert*-butyl alcohol (40 ml) in glacial acetic acid (100 ml). After 5 min, the mixture was diluted with water (500 ml), and extracted with ether. The ether layer was shaken with sodium hydroxide solution. Distillation of the dried extract gave 6 g di-*tert*-butyl sulphide (20 per cent), b.p. 95° to 96° C at 750 mm, n_{20}^{D} 1·3903, in agreement with values recorded by API Project 48 B.

Phenyl ethyl sulphide. Ethyl iodide (7 g) was added slowly to a solution of phenyl mercaptan (5·5 g) and potassium hydroxide (2·8 g) in alcohol (20 ml) and water (3 ml). The mixture was heated under reflux for 20 min, cooled, diluted with 100 ml sodium hydroxide solution, and partially saturated with sodium chloride. The supernatant sulphide was separated. Distillation of the dried product gave 4·5 g phenyl ethyl sulphide (70 per cent), b.p. 200° C at 747 mm, n_{20}^{D} 1·5663.

Pentamethylene sulphide. Pentamethylene dibromide (1 : 5), b.p. 108° to 110° C at 20 mm was prepared from benzoylpiperidine and phosphorus trichloro-dibromide in a modification of the method recorded by V. Braun.[18]

Crystalline sodium sulphide (71 g) in water (70 ml) and alcohol (90 ml) was divided into three parts. One-third was heated under reflux, while the remainder and pentamethylene dibromide (50 g) were added simultaneously from two funnels for over 1 hr. The mixture was heated for 40 min, cooled, diluted with water, and extracted with ether. Distillation of the dried extract gave 16·3 g pentamethylene sulphide (74 per

cent), b.p. 140° to 141·5° C at 740 mm. The sulphide was purified through its mercuric chloride complex, followed by regeneration with sodium sulphide. The yield of pure pentamethylene sulphide was 70 per cent, n_{20}^{D} 1·5046, agreeing with the value of Clark.[19]

This experimental technique is a modification of that recorded by Bennett and Hock,[20] to minimize formation of linear polymers. It appears to give better results than the method of Tarbell, Weaver, and Clay.[21]

Ease of Ring Closure in Formation of Higher-membered Cyclic Sulphides

Five- and six-membered cyclic sulphides are formed by ring closure reactions in high yields. The following preparations were carried out to ascertain the probability of higher-membered cyclic sulphides existing in petroleum fractions.

Hexamethylene Sulphide :

$$EtOOC(CH_2)_4COOEt \longrightarrow HOCH_2(CH_2)_4CH_2OH \longrightarrow Br(CH_2)_6Br \longrightarrow (CH_2)_6S$$

(a) *Hexamethylene glycol.* Ethyl adipate (50 g) in dry ether (200 ml) was added during 2 hr under the usual Grignard conditions to a solution of lithium aluminium hydride (10 g) in ether (300 ml). Excess reagent was decomposed by water, followed by sulphuric acid (30 ml) in water (225 ml). The ether and most of the water were removed by distillation under reduced pressure, and the glycol extracted from the mother liquor by ether–acetone mixture after saturation with magnesium sulphate. Removal of the solvent from the extract gave impure hexamethylene glycol.

(b) *Hexamethylene dibromide.* A mixture of the impure glycol, hydrobromic acid aq 48 per cent wt/vol (100 ml), potassium bromide (10 g), and conc sulphuric acid (30 ml), was boiled under reflux for 5 hr. The solution was diluted with water, the dibromide separated, shaken with sulphuric acid, and rewashed with sodium carbonate solution. Distillation gave 30 g hexamethylene dibromide, b.p. 239° at 760 mm, yield 50 per cent from ethyl adipate.

(c) *Hexamethylene sulphide.* The cyclic sulphide was prepared from hexamethylene dibromide (28 g) and sodium sulphide $Na_2S{\cdot}9H_2O$ (37·5 g) according to the procedure given on p. 712. Steam distillation of the product gave impure hexamethylene sulphide and a non-volatile sulphide polymer as a viscous semi-solid. Redistillation gave 4 g hexamethylene sulphide, b.p. 172° at 760 mm, yield 28 per cent from the dibromide.

Purification. Hexamethylene sulphide (3 g) was added to mercuric chloride (14 g) in warm alcoholic solution (200 ml), and the very insoluble addition compound filtered off, washed with alcohol, and the cyclic sulphide regenerated by steam distillation in presence of sodium sulphide. The product was shaken with sodium carbonate solution and dried. Distillation gave 2·6 g pure hexamethylene sulphide, b.p. 168° at 745 mm, n_{20}^{D} 1·5138. (Found 26·8 per cent S; $C_6H_{12}S$ requires 27·6 per cent S.)

Attempted Preparation of Decamethylene Sulphide

Decamethylene 1 : 10 dibromide was prepared from ethyl sebacate by analogous reactions. Attempted ring closure to the cyclic sulphide gave

only a wax-like polymer. Average molecular weight of the polymer by Rast's method gave values of 548, 548 corresponding to a trimer. $(C_{10}H_{20}S)_3$ requires a molecular weight of 516.

Synthesis of a Cyclic Sulphide in the Kerosine Boiling Range

3 n-*Butylpentamethylene sulphide*

(a) *Ethyl butyl malonate.* This compound was prepared in 70 per cent yield, according to the directions given in *Org. Synth.*, I, 250. Product had b.p. 140° to 145° at 40 mm.

(b) *Ethyl butyl-2 cyanoethyl malonate.* Preparation was carried out from acrylonitrile (7·4 g), ethyl butylmalonate (30 g), and 30 per cent methanolic potassium hydroxide (0·8 g), according to the directions of Ansell and Hey.[23] Yield of ethyl butyl-2 cyanoethyl malonate : 32 g.

(c) 2-*Butylglutaric acid.* Hydrolysis of the nitrile with 48 per cent wt/vol hydrobromic acid aq (300 ml) gave 32 g of crude 2-butylglutaric acid.

(d) *Butylglutaric ethyl ester.* The ester was prepared from crude butylglutaric acid (32 g), ethyl alcohol (80 ml), and conc sulphuric acid (8 ml). Reflux time : 8 hr. Ester (23 g) was isolated by usual procedure.

(e) *Reduction to 2-butylpentamethylene 1 : 5-glycol.* The ester (23 g) in dry ether (100 ml) was added over 40 min to a stirred solution of lithium aluminium hydride (5 g) in ether (150 ml). Excess of reagent was decomposed by water, followed by sulphuric acid (17 ml conc sulphuric acid to 100 ml water). Removal of the ether gave 15 g crude glycol as a viscous oil.

(f) 2-*Butylpentamethylene*-1 : 5 *dibromide.* Prepared from the crude glycol (15 g), hydrobromic acid aq 48 per cent wt/vol (60 ml), potassium bromide (3 g), and conc sulphuric acid (14 ml) by the procedure used for octadecyl bromide. A large amount of insoluble by-product was formed. A quantity of 8·5 g (33 per cent yield) of crude 2-butylpentamethylene dibromide was obtained as a brown oil.

(g) 3-n-*Butylpentamethylene sulphide.* The cyclic sulphide was prepared from the crude dibromide (8·5 g) and sodium sulphide $Na_2S{\cdot}9H_2O$ (10 g), according to the procedure given on p. 712. Steam distillation of the reaction mixture gave 1·0 g (22 per cent) 3-*n* butylpentamethylene sulphide, n_D^{20} 1·4971. A considerable amount of sulphide polymer remained in the flask.

Purification. The sulphide was purified via its dimercuric chloride addition compound, formed in warm alcoholic solution (mercuric chloride 3·4 g, ethyl alcohol 7 ml). On cooling the clear solution, the addition complex separated as a viscous oil, which solidified on further slowly cooling to room temperature. The addition compound was recrystallized from alcohol, and pure 3-*n* butylpentamethylene sulphide (0·5 g) regenerated by steam distillation of the complex with sodium sulphide, followed by washing the thioether with sodium carbonate solution and drying over calcium chloride.

Properties of pure 3-n-*butylpentamethylene sulphide :* b.p. 218° at 760 mm; n_{20}^{D} 1·4884. Analysis : Found 19·5 per cent S, $C_9H_{18}S$ requires 20·2 per cent S.

Dimercuric chloride addition compound : m.p. 97°, solubility 1 g/ml ethyl alcohol at 75°.

The analogous fraction from the Kuwait reactive sulphides gave n_{20}^{D} 1·4840, whilst the solubilities and properties of the mercuric chloride complexes were similar. These results show a wide divergence from pentamethylene sulphide itself; in this case, the mercuric chloride complex is almost insoluble in alcohol.

Acknowledgment

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ALKYLNAPHTHALENES. PART IX.* 1:6- AND 1:7-DIMETHYLNAPHTHALENE

By R. F. Evans † and J. C. Smith † (Fellow)

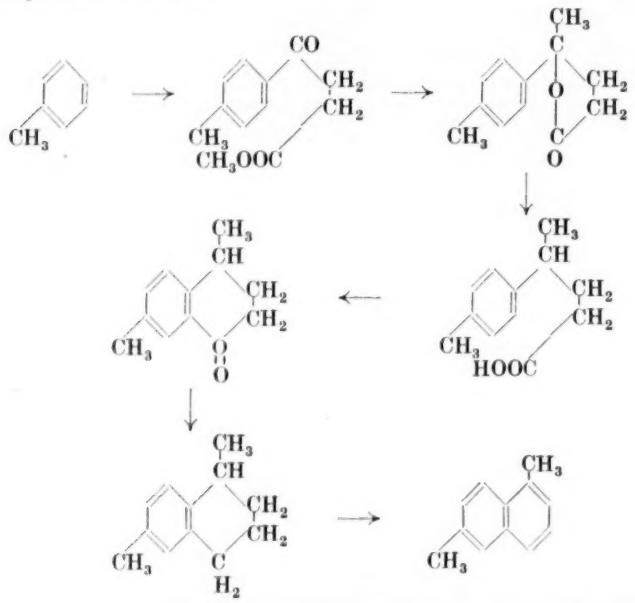
Summary

The preparation of 1 : 6- and 1 : 7-dimethylnaphthalene has been made by unambiguous syntheses and in sufficient amount for thorough purification. The reaction of β-*p*-toluylpropionic ester with a Grignard reagent has been investigated.

Infra-red and ultra-violet spectra of the pure dimethylnaphthalenes are recorded : the 1 : 6-isomer has a characteristic intense band at 787 cm^{-1}. Other physical properties are tabulated and compared with the values in the literature.

1 : 6-Dimethylnaphthalene

Besides occurring in coal tar [1] and petroleum,[2, 2a, 2b] this hydrocarbon is also formed as a pyrolysis product of vitamin A,[3] and has been obtained in the dehydration of ionone.[4]



* MS received 16 February 1953. The summarizing paper [4a] is to be regarded as Part VIII of this series.

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The synthesis achieved by Kipping and Wild,[5] and confirmed by Bailey *et al*,[6] gives a low overall yield. In this investigation a more convenient route was explored in 1948 (also by Dev [7]), and the details of the improved preparation are now given. The physical properties, including the ultra-violet and infra-red spectra, are recorded for a highly purified specimen.

By the succinic anhydride method toluene yields β-*p*-toluylpropionic acid. The critical stage of the synthesis is the introduction of a methyl at the carbonyl group. Normally, a CO is much more reactive towards the Grignard reagent than is an ester group, but here the CO is partly shielded by the aromatic nucleus, and is weakened in ketonic activity by accession of electrons from the *p*-tolyl system. In order to assist the preferential attack on the carbonyl group, the Grignard reagent is slowly added to the ester solution and not vice versa: an excess of Grignard reagent at any moment is thus avoided.[7a]

In spite of the slow addition of the Grignard reagent, there is some attack on the $-COOCH_3$ group (to form *tert*-alcohol); there is also partial hydrolysis of the $COOCH_3$ and loss of water from *tert*-alcoholic groups. The β, γ-unsaturated pentenoic acid [8] in this mixture is easily extracted with sodium carbonate solution, regenerated with acid, and lactonized by heating with hydrochloric acid. In Table I the effect of varying the amount of Grignard reagent is set out. After further hydrolysis of the esters, extraction of the alkaline hydrolysate with ether removed neutral products, and then further amounts of the desired γ-hydroxy-γ-(*p*-tolyl)-pentanoic acid were isolated as the lactone. Reduction of the lactone with hydriodic acid and phosphorus, or of the sodium salt of the hydroxy-acid with hydrogen and copper chromite,[9] gave γ-(*p*-tolyl)valeric acid.

TABLE I

Mol Grignard agent to mol keto-ester	Yields %			Yield % of (*a*) based on keto-ester reacted
	(*a*) Unsaturated acid + lactone	(*b*) Glycol	(*c*) Recovered keto-acid	
1·4	67	5·4	18·2	82
1·4	75	8	10·5	87
1·45	60	10·6	12·8	77
1·5	62	10·3	22·9	81
1·7	65	11·2	22·4	83
1·7	71	10·8	12·2	82
1·9	55	18·4	11·1	65

Ring closure of the saturated acid to the tetralone proceeded smoothly by the phosphoric acid–phosphorus pentoxide method previously developed (Part VI [13]). Unfortunately, the tetralone was a liquid which could not be induced to crystallize.

Reduction of the tetralone to the tetralin, followed by catalytic dehydrogenation, gave excellent overall yields of 1 : 6-dimethylnaphthalene. The naphthalene was, as a preliminary purification, converted into the sharp-melting picrate. This should have eliminated any unchanged tetrahydrodimethylnaphthalene, and the regenerated dimethylnaphthalene

was obtained in quantity (100 cc) sufficient for fractionation with a Stedman column. From the time–temperature curve (Fig 1) obtained with the

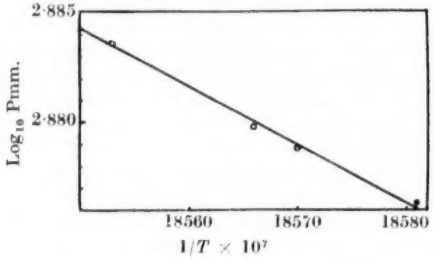


FIG 1

1 : 6-DIMETHYLNAPHTHALENE

Rossini apparatus, it was apparent that the sample was of high purity. The physical properties recorded were: b.p. 265·6° at 760 mm; f.p. −16·6°; D_4^{20} 1·0023; n_D^{20} 1·6072; $[R_L]_D^{20}$ 53·84, with exaltation 2·96.

EXPERIMENTAL

β-(p-*Toluyl*)*propionic acid*. Toluene was purified by being shaken several times with conc sulphuric acid, then with alkali prior to fractional distillation through a twenty-five-plate Stedman column. The fraction, b.p. 110·6° at 760 mm, n_D^{20} 1·4950 (literature n_D^{20} 1·49693), may have contained traces of non-aromatic hydrocarbons, but these could take no part in the succinoylation.

Powdered aluminium chloride (401 g, 3 mol) was added gradually during 1 hr with swirling to a mixture of succinic anhydride (150 g, 1·5 mol), toluene (180 cc, 1·7 mol, n_D^{20} 1·4950), and tetrachloroethane (600 cc, recently distilled). After standing 36 hr, the mixture was decomposed by addition of ice and conc hydrochloric acid (260 cc). The organic liquids were removed by steam distillation, and the residue, after cooling and filtering, was extracted several times with sodium carbonate solution.

Acidification of the carbonate extracts precipitated 296 g of product m.p. 121° to 124°. The theoretical yield was 288 g, so that the precipitate contained inorganic matter. Four recrystallizations from benzene produced a sample of keto-acid, m.p. 127° to 128·2° (literature m.p. range from 117° [10] to 130° [7]). The methylester, obtained in 94 per cent yield from the acid (400 g), methanol (800 cc), and conc sulphuric acid (40 cc) after refluxing 6 hr, boiled at 177° to 178° at 12 mm, and had m.p. 50°. Limpricht [11] gives m.p. 43°.

A preparation of β-(*p*-toluyl)propionic acid modelled on the Organic Syntheses procedure [11a] for β-benzoylpropionic acid gave a 93 per cent yield of product, m.p. 122° to 125°.

γ-(p-*Tolyl*)*pent-3-enoic acid*. A simple method was devised for carrying out the addition of the Grignard reagent to the ester solution. A two-necked, 2-litre flask was fitted with an adaptor carrying a reflux condenser closed with a calcium chloride tube, and a mercury-sealed stirrer. The

side-neck of the flask bore a separating funnel fitted with (*a*) a calcium chloride tube, and (*b*) a delivery tube leading to the bottom of the flask. In the end of this delivery tube some glass wool was loosely packed to act as a filter.

The Grignard solution (1·4 mol) was formed from magnesium (16·8 g), methyl iodide (50 cc), and ether (150 cc) and then sucked through the filter into the funnel; the flask was washed twice with a little ether, each washing being sucked up into the funnel. This Grignard solution was added during 3·5 hr to a stirred, cold (*ca* −2°) solution of methyl β-(*p*-toluyl)propionate (103 g, 1·0 mol) in ether (515 cc) in the flask used to prepare the Grignard reagent. After standing at room temperature for 2 hr, the mixture was refluxed for 4 hr (this was known to cause almost complete hydrolysis of the methyl ester grouping) and left overnight. Decomposition with 10 per cent hydrochloric acid gave two clear layers. From the ethereal layer sodium carbonate solution extracted the acidic products (62·5 g, 66 per cent yield, calculated as γ-(*p*-tolyl)pent-3-enoic acid). The non-acidic products of the Grignard reaction remaining in the ethereal layer were concentrated by distillation, and were hydrolysed (in case any ester remained) by boiling for 4 hr with aqueous-alcoholic potassium hydroxide. The alkaline solution was freed from unsaponifiable substances (glycol, etc) by ether extraction and then boiled with 12 per cent hydrochloric acid. 8·9 g (8 per cent) of glycol and its dehydration products were isolated from the ether solution. The hydrochloric acid layer was extracted with ether, the ethereal extract washed with carbonate, dried, and distilled. 10 g (9 per cent) of γ-methyl-γ-tolylbutyrolactone were obtained. Acidification of the carbonate extracts precipitated 11·7 g (11 per cent) of unchanged β-(*p*-toluyl)propionic acid.

All the unsaturated acid (γ-*p*-tolyl-pent-3-enoic acid) was converted into the lactone, b.p. 182° to 183° at 13 mm, by boiling with 16 per cent hydrochloric acid. Unchanged acid was removed and again heated. A sample crystallized from benzene–light petroleum melted at 49° to 51°. Johnson and Jones [9] give m.p. 51° to 52°.

γ-(p-*Tolyl*)*pentanoic acid*. (*a*) Lactone (10 g, m.p. 49° to 51°), hydriodic acid (60 cc of D 1·7), and red phosphorus (8 g) were refluxed for 6·5 hr. After diluting with water and filtering from solids, the liquid was extracted with ether, yielding 1·1 g of lactone and 8·1 g of crude saturated acid. Crystallized from light petroleum and then from aqueous methanol, the product melted at 25° to 27°.

(*b*) Lactone (84 g) was refluxed for 2 hr with sodium hydroxide (19 g) in water (500 cc) and sufficient ethanol to give a clear solution. The solution was then distilled while water was added, until all alcohol had been removed, and the volume made up to 950 cc (giving a N solution of sodium hydroxide). Glacial acetic acid was added until the liquid was faintly acid to litmus. This solution was then hydrogenated at 185° with hydrogen at 190 atm and copper chromite (14 g) for 5 hr, yielding 10·9 g of unattacked lactone and 62·5 g (86 per cent yield) of saturated acid, m.p. 30°. Values in the literature are 32°,[8] 30° to 31°,[12] and 28° to 30·5°.[9]

4 : 7-*Dimethyl*-1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. γ-(*p*-Tolyl) pentanoic acid (59·5 g) was added to a hot (160°) solution of phosphorus pentoxide (179 g) in phosphoric acid (200 cc of D 1·75).[13] The reaction was

complete in 2·5 min, and the mixture was poured into water. Ether extraction of the cold mixture gave a red layer which, after washing with water and with sodium carbonate solution, was dried over sodium sulphate and distilled. The fraction of b.p. 152° to 155° at 13 mm (47·4 g, 88 per cent yield) was collected, and a solid residue remained. From this residue, a colourless product was obtained by passage in benzene solution through an alumina column and a band developed which fluoresced in ultra-violet light. After four crystallizations from ethanol the solid melted at 219° to 220° (decomp). (Found : C, 90·94; H, 8·84 per cent. $C_{24}H_{28}$ requires C, 91·06; H, 8·94 per cent.) The structure of this by-product will be discussed in a later communication.

As the tetralone could not be crystallized, it was redistilled and then reduced by the Huang–Minlon procedure.

1 : 6-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. 4 : 7-Dimethyl-1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (45·3 g), sodium hydroxide (39·1 g), and hydrazine hydrate (55 cc of 60 per cent) were refluxed with ethylene glycol (200 cc) and diethylene glycol (250 cc) for 2 hr in order to form the

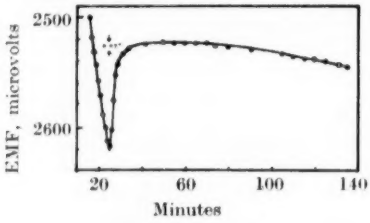


FIG 2

1 : 6-DIMETHYLNAPHTHALENE

hydrazone. After water had been allowed to distil (this distillate was collected) the mixture was refluxed at 200° (air-condenser) for a further 6 hr. Extraction of the cold reaction mixture and the previously collected aqueous distillate with light petroleum gave a fluorescent liquid, which was washed with water, conc hydrochloric acid (twice), sodium carbonate solution, and then dried. On distillation the fraction of b.p. 111° to 112° at 14 mm (35·4 g, 85 per cent yield) was collected. On redistillation it boiled at 238° to 240° at 755 mm, and had n_D^{20} 1·5307; D_4^{20} 0·9484 : $[R_L]_D^{20}$ 52·25, with exaltation 0·43. Attempts to freeze the liquid failed. Dev [7] gives neither physical constants nor analytical figures for this substance. Found : C, 90·70; H, 9·97 per cent. $C_{12}H_{16}$ requires C, 89·96; H, 10·07 per cent.

1 : 6-*Dimethylnaphthalene*. The dimethyltetrahydronaphthalene was dehydrogenated by heating at 200° to 240° with palladized charcoal (30 per cent Pd), and the product was isolated as picrate, m.p. 110° to 111°. Regeneration from the picrate with 3 per cent sodium hydroxide solution and distillation of the product gave, in all, 93·5 g (91 per cent yield) of colourless liquid, b.p. 140° at 19 mm, n_D^{20} 1·6072.

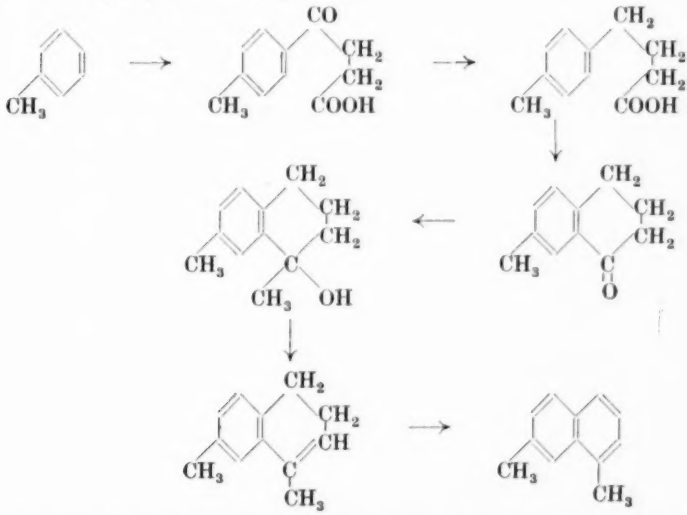
Fractionally distilled with a Stedman column (under reduced pressure with a take-off rate of 16 : 1), it gave a large constant-boiling fraction of

b.p. 138° at 18 mm, 265·6° at 760 mm; n_D^{20} 1·6072; D_4^{20} 1·0023; $[R_L]_D^{20}$ 53·84, with exaltation 2·96. The f.p. was obtained in the Rossini apparatus used in Part VI [13] of this series.

Supercooling prior to freezing was considerable, and recovery was slow. The sample had actual f.p. −16·9°, and the f.p. of 100 per cent material estimated by the geometrical construction of Glasgow *et al* [14] was −16·6°. Figs 1 and 2 show the curves for b.p. (temperature against pressure) and for f.p. (time against temperature). The physical constants agree well with those quoted for the small-scale preparation of Bailey *et al*,[6] m.p. −17° to −15°, b.p. 264°, n_D^{20} 1·6072. Nametkin *et al*,[2a] who isolated this hydrocarbon from Surakhan petroleum, quote f.p. −16° to −18°, b.p. 263° to 265°, $n_D^{23·5}$ 1·6053.

1 : 7-Dimethylnaphthalene

This hydrocarbon has been isolated from both coal-tar and petroleum [2b, 15, 16, 17] and has also been synthesized in various ways. All but two of those syntheses gave a liquid product. In Part I of this series [6] it was suggested that both Zelinsky's [18] hydrocarbon of m.p. 107° and Veselý and Medvedeva's [19] substance of m.p. 84° to 85° were mainly 2 : 6-dimethylnaphthalene (m.p. 110°).



The succinic anhydride route from toluene, first used by Barnett and Sanders,[20] and repeated in Part I,[6] has been improved in the larger-scale synthesis here described. Phosphoric acid has been used for the ring closure of the arylbutyric acid, methylmagnesium chloride instead of the iodide in the methylation of the carbonyl group of the tetralone, and copper sulphate at 100° for the dehydration of the resulting tetralol.

After the dimethylnaphthalene had been synthesized from intermediates purified at every stage, the experiment was made of purifying at only two

stages, the tetralone (m.p. 33°) and the dimethylnaphthalene picrate (of m.p. 118° to 119°). This resulted in a saving of time and materials without appreciable loss of purity in the final product. All specimens of the hydrocarbon crystallized too slowly on cooling for equilibrium to be established between solid and liquid; only the melting-curve was relied upon as a measure of the purity. A low rate of crystallization is often

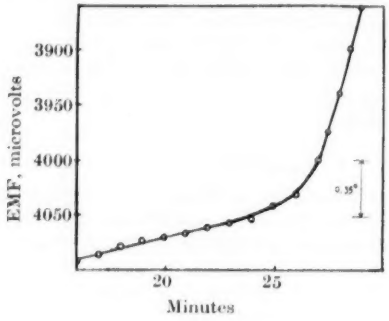


FIG 3

1 : 7-DIMETHYLNAPHTHALENE
(2nd form)

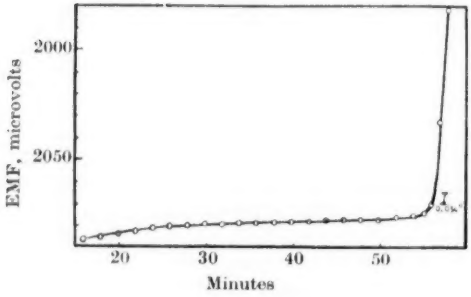


FIG 4

1 : 7-DIMETHYLNAPHTHALENE
(Stable form)

observed with polymorphous substances, and it was found that this hydrocarbon could exist in two solid forms : after cooling rapidly to −32° and only then being stirred, the liquid began to crystallize slowly. The time–temperature curve for the warming mixture showed an inflexion at −27·6°; the stable form melted at −13·89° (Figs 3 and 4).

EXPERIMENTAL

γ-(p-Tolyl)butyric acid. The pure β-(*p*-toluyl)propionic acid of m.p. 128·2° (see under 1 : 6-dimethylnaphthalene), reduced by the Clemmensen method as in Part VI,[13] gave 97 per cent yields of product which, after one

crystallization from light petroleum (b.p. 60° to 80°), melted at 60° (literature : 59°,[20] 61° to 62°[21]). Five lots of impure keto-acid (100 g each and

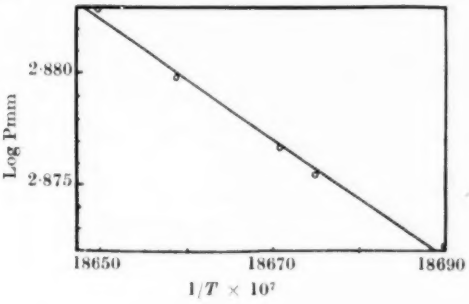


FIG 5

1 : 7-DIMETHYLNAPHTHALENE

m.p. 121° to 124°) similarly reduced gave a product of m.p. 47° to 52° in average yield of 92 per cent.

7-Methyl-1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. γ-(*p*-Tolyl)butyric

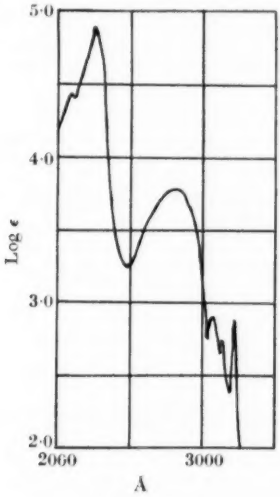


FIG 6

1 : 6-DIMETHYLNAPHTHALENE

Ultra-violet spectrum in methanol

acid (20 g of m.p. 59·5°) was added to a solution of phosphoric oxide (80 g) in phosphoric acid (60 cc of *d* 1·75) kept at 150° to 155° and the mixture stirred vigorously for 5 min. After cooling, followed by pouring into water,

the mixture was extracted with ether; it yielded 16·7 g (92 per cent) of tetralone, b.p. 145° to 155° at 11 mm, m.p. 32·5° to 33·5°.

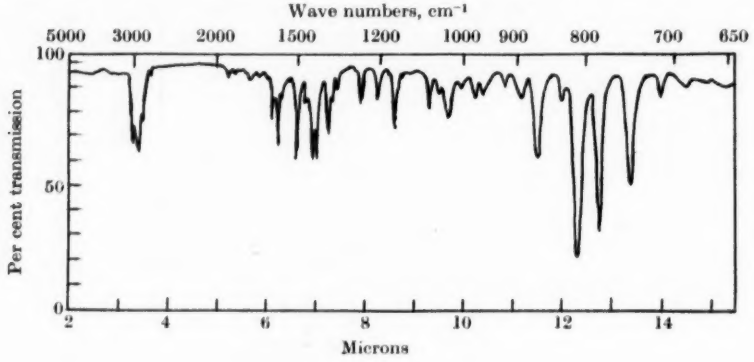


FIG 7

1 : 6-DIMETHYLNAPHTHALENE

Infra-red spectrum (l = 0·01 mm)

Similarly, the impure γ-(p-tolyl)butyric acid (80 g of m.p. 47° to 52°) and a solution of phosphoric oxide (240 g) in phosphoric acid (267 cc of d 1·75) kept 3 min at 155° gave 64·7 g (90 per cent yield) of liquid, b.p. 137° to

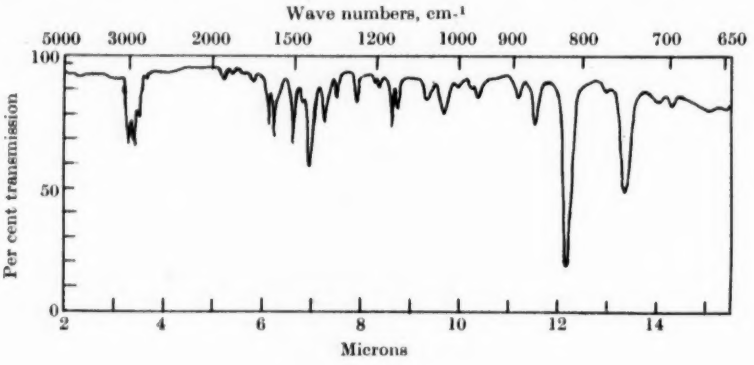


FIG 8

1 : 7-DIMETHYLNAPHTHALENE

Infra-red spectrum (l = 0·01 mm)

138° at 10 mm, which quickly solidified. 274 g of tetralone were crystallized systematically from purified light petroleum (b.p. 40° to 60°) to yield a product of constant m.p. 33·1° In the literature the recorded m.p. are : 31° to 33°,[22] 32·5° to 33°,[23] 35°,[20] and 35° to 36°.[24]

The *oxime* crystallized from light petroleum in colourless rhombohedra, m.p. 98° to 99°. (Found: C, 75·4; H, 7·6 per cent. $C_{11}H_{13}NO$ requires C, 75·4; H, 7·5 per cent.)

4 : 6-*Dimethyl*-1 : 2-*dihydronaphthalene*. By the usual procedure 24 g of tetralone (m.p. 33·5° to 34°) reacted with methylmagnesium iodide to yield the carbinol, and this was dehydrated by refluxing with formic acid (85 per cent). The resulting oil distilled at 114° to 123° at 11 mm, weighed 15·9 g (67 per cent yield) and had n_D^{20} 1·5680.

Methyl chloride was bubbled into a refluxing mixture of magnesium (33·6 g, 2 g atoms), ether (500 cc), and a little methyl iodide for 5 hr. An ethereal solution of the tetralone (112 g, 1 mol, in 336 cc) was slowly added over 45 min to the well-stirred, ice-cold Grignard solution. Later, the mixture was refluxed 1 hr and then left overnight. It yielded a solid product (the carbinol) which was heated with anhydrous copper sulphate (97 g) on a boiling water-bath for 2 hr. The brown oil, isolated with the aid of ether, distilled at 118° at 12 mm (97·5 g, 88 per cent yield) and had n_D^{20} 1·5694.

1 : 7-*Dimethylnaphthalene*. The combined purer specimens of dimethyldihydronaphthalene (19·7 g) and palladized charcoal (1·3 g) were heated so that the mixture just refluxed while a slow stream of nitrogen was passed. As the dehydrogenation proceeded, the b.p. rose from 248° to 262° within 2 hr and was continued ½ hr longer. Distillation gave 18·6 g (96 per cent yield) of dimethylnaphthalene, b.p. 261° to 263°. Redistillation with a precision column gave a main fraction of n_D^{20} 1·6074.

TABLE II

Physical Properties of 1 : 7-*Dimethyl Naphthalene*

Isomer	M.p., °C	B.p., °C at 760 mm	n_D^{20}	d_4^{20}	Authors
1 : 7-	−13·89 and −27·6	262·8	1·6076	1·0016	Present
	−14 and −28·5	263	1·6072		Bailey *et al* [6]
		261–262	1·6083		Kruber and Schade [16]
1 : 6-	−16·9 −16·6 *	265·6	1·6072	1·0023	Present
	−17 to −15	264	1·6072		Bailey *et al* [6]
	−18 to −16	263–265	1·6067 *	1·0013	Nametkin *et al* [3a]
		262–263			Kipping and Wild [5]

* Calculated

Dehydrogenation of the less pure dimethyldihydronaphthalene (50 g) with palladized charcoal (2·5 g of 10 per cent Pd) was almost complete after 5 hr refluxing, and gave a 95 per cent yield of liquid having n_D^{20} 1·6040. When 115 g of crude dimethylnaphthalene (n_D^{20} 1·604) were slowly added to a refluxing ethanolic solution of picric acid (149 g in 400 cc), the mixture

deposited on cooling a yellow picrate which, washed with ethanol and left several days spread on paper, weighed 237 g and melted at 118° to 119°. From the ethanolic mother liquor crude dimethylnaphthalene was recovered. After dehydrogenation it yielded (with picric acid) 35·5 g of picrate, m.p. 118° to 119°.

The combined samples of picrate were decomposed with sodium hydroxide solution in presence of light petroleum (b.p. 60° to 80°) giving 96 g (84 per cent yield) of liquid, b.p. 126° to 128° at 13 mm, n_D^{20} 1·6075. Fractional distillation at 13 mm with a Stedman column gave a middle fraction of b.p. 262·8°, n_D^{20} 1·6076, and d_4^{20} 1·0016. $[R_L]_D^{20}$ was therefore 53·95 and exaltation 3·07.

Acknowledgments

The authors are indebted to the Department of Scientific and Industrial Research and to the Institute of Petroleum for grants to one of them (R. F. E.). They wish to thank Dr F. B. Strauss for recording the spectra (see Appendix).

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APPENDIX

Spectra of 1 : 6- and 1 : 7-Dimethylnaphthalene

By Dr F. B. Strauss *

The absorption spectra in the ultra-violet were measured by means of a UNICAM spectrophotometer. The appearance of the ultra-violet absorption curves of the two compounds is very much alike, and only one of them is shown. Methanol was used as a solvent. (Fig 6.)

The exact positions of the absorption peaks and their molar extinction coefficients are listed separately for both compounds.

1 : 6-Dimethylnaphthalene		1 : 7-Dimethylnaphthalene	
λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
2100	26,310		
2250	77,500	2265	92,000
2800	5840	2800	6120
3075	764	3075	641
3144	521	3150	367
3225	749	3222	508

The absorption spectra in the infra-red were measured by means of a Perkin–Elmer Model 21 double-beam spectrophotometer, fitted with a rocksalt prism. The spectra were taken of the samples in their liquid phase at room temperature, at a cell length of 0·01 mm. (Figs 6 and 7.)

The most conspicuous differences between the spectra of the two compounds are shown in the region of the C–H deformation frequencies. While both compounds have intense bands at 750 and 815 cm^{-1}, 1 : 6-dimethylnaphthalene has an additional intense band at 787 cm^{-1}.

* The Dyson Perrins Laboratory, Oxford.

THE INSTITUTE OF PETROLEUM

ANNUAL REPORT

For the Year Ending 31 *December* 1952

Mr H. S. Gibson took office as President after the Annual General Meeting in succession to Mr C. A. P. Southwell, to whom the thanks of the Institute were accorded for his valuable services during his two-year period of office.

Membership

Details of membership as at 31 December 1952 :—

	Total 31 Dec. 1951	Change during 1952						Total 31 Dec. 1952
		New	Transferred to	Lapsed and resigned	Deceased	Transferred from	+ or −	
Hon. Members	3	—	—	—	—	—	—	3
Hon. Fellows	6	—	—	—	1	—	− 1	5
Members	605	27	8	25	5	9	− 4	601
Fellows	553	22	11	10	8	—	+ 15	568
Associate Members	768	89	4	34	5	13	+ 41	809
Associate Fellows	571	168	35	14	3	1	+185	756
Students	146	37	—	18	—	35	− 16	130
Totals	2652	343	58	101	22	58	+220	2872
Member-Companies	174	9	—	4	—	—	+ 5	179

The net increase in membership during the year has been gratifyingly larger than of recent years, and Council wishes to express its appreciation to the many members who have brought this about.

It is hoped that an even greater increase in membership can be attained in 1953. Council has constantly in mind the need for covering the widest possible fields of interests of the industry in the activities of the Institute, and plans to this end include the proposal to enlarge the *Review*—a publication which finds increasing acceptance among members.

Deaths

The following deaths during 1952, are recorded with regret :—

R. E. Andrews (A.M.)
F. C. Baker (M.)
R. A. Baldry (A.M.)
E. Bottomley (A.M.)
J. S. S. Brame (Hon.F.)
Iain Cameron (F.)
L. D. Derry (A.F.)
H. de Wilde (F.)
J. S. A. Don (A.M.)
L. G. Gabriel (F.)
J. S. Gemmill (A.F.)
J. T. Guthrie (F.)
H. C. Hawkins (A.F.)
H. Healey (M.)
W. H. Huxley (F.)
H. W. Lane (M.)
R. Levi (F.)
J. G. Muller (M.)
J. M. Penney (F.)
D. G. Pidgeon (A.M.)
J. L. Taylor (F.)

Professor J. S. S. Brame was a member of Council and Vice-President from 1918 to 1921. In the latter year he was elected President, and held office for two years. He was elected an Honorary Fellow in 1951.

Mr H. de Wilde was a member of Council from 1947 to the date of his death.

General

Premises

A new lease of Manson House was signed during the year for a further ten years.

General Meetings

Twelve Ordinary General Meetings were held, and Mr C. A. P. Southwell presented his Presidential Address after the Annual General Meeting.

The recorded average of ninety-six in attendance at meetings represented a considerable improvement over previous years (fifty for 1949; eighty for 1950; seventy-eight for 1951). The actual attendance normally exceeds that recorded. Approximately 40 per cent of those attending were visitors, introduced by members, who are always welcome at the ordinary meetings.

Annual Dinner

The Annual Dinner was again held at Grosvenor House, the principal speaker being Marshal of the Royal Air Force, the Lord Tedder, G.C.B., D.C.L., LL.D.

The attendance reached the record figure of 860.

Summer Meeting

A very enjoyable Summer meeting was held at Hastings in June. Seventy-six members and their wives attended, and three talks were given under the general theme "Oil—The Task Ahead."

The success of this meeting has encouraged the Council to organize a similar meeting with a rather more ambitious programme at Buxton in June 1953.

Studentship

Mr D. Shearn was elected to the Annual Scholarship offered by the Institute at Birmingham University, and Mr J. Lacy was awarded the Institute of Petroleum Prize at the Imperial College of Science and Technology.

Aviation Products Data

Drafting of the Data Sheets on Aviation Lubricating Oils has been completed, and copies have been sent to the Royal Aeronautical Society, under whose auspices, jointly with the Institute, the data sheets are published. The Aviation Fuels Data Sheets are being brought up to date as necessary.

By-laws

The proposal to operate a covenant scheme for the payment of subscriptions by members necessitated minor changes in the Articles of Association (Article 8) and the By-laws (By-law 41) in order to meet the requirements of the Inland Revenue. These changes were approved at

a Special General Meeting in June, but the introduction of the scheme has had to be postponed, pending clarification of the legal position of such schemes.

At the same meeting a change was agreed in Bye-law 72, whereby ballot papers for elections to Council would in future be sent to all members, and not merely to those resident in the United Kingdom.

There was also a change in By-law 28, whereby unsuccessful candidates for admission to or transfer within the Institute could be notified of the result of their application, such notifications having previously been specifically barred.

Branches and Students' Section

Branch activities were kept up and increased during the year. A very satisfactory level of attendances at meetings was reported from all Branches.

Arrangements were made for Mr E. A. Evans, as Branch Lecturer, to visit all Branches during the sessions 1952–53 and 1953–54.

Correspondence was exchanged with both Ireland and Australia relating to new Branches being formed, although in neither case have the discussions proceeded to the stage when a formal request for authority to form a Branch can be submitted to Council.

Engineering

The Engineering Committee has continued the preparation of the Marketing, Refining, and Production Safety Codes. These Codes involve a great deal of detailed work, but good progress is being made, and it is hoped that these Codes will be ready for publication at the end of this year. Consideration is also being given to the revision of the Electrical Code.

Avonmouth Fire Report

A Sub-Committee was set up in March 1952 to consider the implications of the report on the Avonmouth Fire made by Dr H. E. Watts, H.M. Chief Inspector of Explosives, as some of his recommendations appeared to be at variance with those in the draft Marketing Code. The Sub-Committee submitted its observations to the Engineering Committee in July 1952, and these have since, with the support of H.M. Chief Inspector, received wide publication.

Finance

Our Revenue Account showed a very small surplus on the year's operations. Total income was about £760 more than in 1951, but administration and establishment expenses were also about £700 greater.

Income from members' subscriptions was £17,830, compared with £17,220 in 1951 and £16,630 in 1950.

Expenditure (excluding that on publications) rose by about £720 and stood at nearly £17,000. Salaries and pensions increased by £430; and purchase of library literature (at £250) by £125.

The Institute spent £24,250 in 1952 in the printing and publishing of its various publications. Against this, revenue from sales and advertising

was only £18,000, but the value of stocks of publications increased by over £4,800 over the year.

Members may be interested to learn that the bare cost of printing the monthly issues of the *Journal* and the *Review* were as follows :—

1952	£11,225
1951	£8,956
1950	£6,940

Against an increase in production costs of £4,285 during the last two years, revenue from advertisements rose by £1,475. Thus the increased income resulting from the new membership subscription rates, introduced about three years ago, has been completely absorbed in the higher costs of providing members with the two monthly periodicals.

Publications

Journal

Volume 38 of the *Journal* was published in twelve monthly parts, and contained 1002 pages of transactions (749 pages in 1951) and 680 pages of abstracts (596 in 1951), an aggregate of 1682 pages (1345 in 1951), excluding the usual indexes and title pages.

Transactions

The total number of papers in the *Journal* was fifty-eight and, on a very broad classification, their subject matter was concerned with :—

Field and production	1
Chemistry and physics	14
Analysis and testing	19
Utilization	21
General	2
Economic	1

Abstracts

In comparison with 1951, the number of abstracts published was higher by 509, an increase of 18·4 per cent.

The numbers of abstracts in the main classes were :—

	1951		1952	
	No.	Per cent	No.	Per cent
Exploration and exploitation	874	31·7	836	25·6
Transport and storage	172	6·2	163	5·0
Refining operations	491	17·8	801	24·5
Products	837	30·3	1001	30·6
Corrosion	110	3·9	125	3·8
Engines and equipment	126	4·6	126	3·8
Safety precautions	37	1·3	38	1·1
Miscellaneous	115	4·2	181	5·6
Total	2762	100·0	3271	100·0

This section of the *Journal* also contained critical reviews of fourteen

new books, references to sixty-three books added to the library by presentation or purchase, and references to fifty-two British standards.

Other Publications

During 1952 seven books were issued : the " Report of the Oil Shale and Cannel Coal Conference," " Standard Methods " (12th edition), the " Petroleum Measurement Manual," " Reviews of Petroleum Technology "—volumes 11 (1949) and 12 (1950), the " Report of the Conference on Mass Spectrometry," and the British volume of the " ASTM/IP Petroleum Measurement Tables." These tables were produced in collaboration with the American Society for Testing Materials.

At the close of the year the publication work in progress included the 13th edition of " Standard Methods," volume 13 of " Reviews of Petroleum Technology," the metric volume of the " ASTM/IP Petroleum Measurement Tables," and a second edition of " Modern Petroleum Technology." The Publications Section are also concerned with the organization and collection of papers for the IP Summer Meeting 1953, and for the 4th World Petroleum Congress to be held in Italy in 1955.

Library

Work on the reclassification of the contents of the Library is proceeding.

Research

The Hydrocarbon Research Group has continued to sponsor research work at various universities.

Research Group No. 2 has been collaborating during the year with the Medical Research Council on the biological relationships of petroleum, and a provisional report of the work of the group is being submitted to this Council in the near future.

Standardization

Active co-operation with ASTM has continued, and progress has been made in improving agreement between ASTM and IP Methods. Mr K. G. Mackenzie and Mr L. C. Burroughs, both members of the ASTM D-2 Committee, were elected honorary members of the IP Standardization Committee. Early in the year the ASTM D 2 Committee appointed six of its members to the IP Standardization Committee. The IP became official members of ASTM D-2, and nominated six representatives to serve on the latter Committee.

Useful discussions with representatives of the Bureau de Normalisation du Pétrole have, it is hoped, laid the foundations for mutual co-ordination of work on the standardization of test methods.

Five new methods have been drafted, and technical revisions have been made in thirty methods.

Further progress has been made in redrafting methods to make them more readily usable in countries employing the metric system, and to improve the presentation of precision limits; only about 10 per cent now remain to be redrafted in this way.

Acknowledgments

Throughout the year, the staff has continued to serve the Institute well. Council considers itself most fortunate to have such an efficient and loyal team, who, headed by the General Secretary and supported by the Editor and other senior members of the staff, are so largely responsible for the achievements which can be recorded for 1952.

By order of the Council,
C. Chilvers, Honorary Secretary.

March 1953.

Note: The report of the 40th Annual General Meeting at which the Annual Report and Accounts for 1952 were presented appears on pp. 381–2.

THE INSTITUTE

(A Company limited by Guarantee

BALANCE SHEET AS

1951 £	CAPITAL AND RESERVES	£ s. d.	£ s. d.
	Capital of the Institute under Bye-laws 36, 44, and 45 :—		
	Life Membership Fund—		
	As at 31 December 1951	939 6 6	
	Add Receipts during 1952	69 11 3	
939		1,008 17 9	
	Entrance and Transfer Fees—	£ s. d.	
	As at 31 December 1951	6,173 12 9	
	Add Receipts during 1952—		
	Entrance Fees	367 10 0	
	Transfer Fees	10 10 0	
6,174		6,551 12 9	
	Profit on Sale of Investments—		
258	As at 31 December 1951	257 19 4	
	Donations—		
326	As at 31 December 1951	326 5 0	
7,697			8,144 14 10
5	**T. C. J. Burgess Prize Fund**		5 0 0
1,702	**General Reserve (previously War Contingencies Reserve)**		1,702 0 11
	Revenue Account :—		
	As at 31 December 1951	10,376 1 6	
	Add Surplus for year to date	80 0 6	
10,376			10,456 2 0
	Subscriptions Received in Advance :—		
	Members' Subscriptions for 1953	1,715 12 9	
	Member Companies' Subscriptions for 1953	10 10 0	
	Journal Subscriptions for 1953	1,072 0 4	
	Journal Subscriptions for 1954	13 3 4	
2,511			2,811 6 5
	Current Liabilities :—		
	Sundry Creditors and Accrued Charges	5,388 9 11	
	World Petroleum Congress	29 6 6	
	Entertainment Account—	£ s. d.	
	As at 31 December 1951	317 0 2	
	Add Excess of Receipts over Expenditure during year to date	30 13 0	
		347 13 2	
1,767			5,765 9 7
110	**Sum Set Aside for Grants to Branches and Students' Section**—unallocated		167 0 0
£24,168			£29,051 13 9

Approved by the Council :—
H. S. GIBSON, *President.*
G. H. COXON, *Hon. Treasurer.*

AUDITORS' REPORT TO THE MEMBERS

We have examined the above Balance Sheet and annexed Revenue Account and report that we have for the purposes of our audit. In our opinion proper books of account have been kept by the Institute, so agreement with the books of account. In our opinion, and to the best of our information and according to manner required, and the Balance Sheet gives a true and fair view of the state of the Institute's affairs at on that date. We have accepted a Certificate from the Institute's Bankers for the Securities held by them

116 OLD BROAD STREET, LONDON, E.C.2.
31 *March* 1953.

OF PETROLEUM

and not having a Share Capital)

AT 31 DECEMBER 1952

1951 £	ASSETS	£ s. d.	£ s. d.
	Investments :—		
	On Account of Capital, at cost—		
	£525 0 0 3% Savings Bonds, 1955/65	525 0 0	
	867 8 6 2¾% Bristol Corporation Redeemable Stock, 1955/65	845 17 7	
	150 0 0 3% Smethwick Corporation Redeemable Stock, 1956/58	151 4 9	
	150 0 0 3% Luton Corporation Redeemable Stock, 1958	151 6 7	
	806 8 3 3% Manchester Corporation Redeemable Consolidated Stock, 1958	845 17 7	
	600 0 0 3% Bristol Corporation Redeemable Stock, 1958/63	597 7 3	
	664 6 6 3% London County Consolidated Stock, 1920	481 10 6	
	400 0 0 3% Metropolitan Water Board "A" Stock, 1963	346 10 7	
	193 0 0 3% British Gas Guaranteed Stock, 1990/95	154 8 6	
	156 9 8 3% British Transport Guaranteed Stock, 1978/88	105 4 9	
	461 0 0 2½% Funding Loan, 1956/61	461 15 6	
	500 0 0 2½% Defence Bonds	500 0 0	
5,166			5,166 3 7
	(Market Value at 31 December 1952, £4,656.)		
2,531	Cash on Deposit with Post Office Savings Bank		2,978 11 3
7,697			8,144 14 10
	On Account of Revenue, at cost—		
	£2,942 2 9 3% Savings Bonds, 1955/65	2,975 0 0	
	2,000 0 0 3% Savings Bonds, 1960/70	2,000 0 0	
4,975			4,975 0 0
	(Market Value at 31 December 1952, £4,387.)		
	Office and Library Furniture at cost, less amounts written off :—		
	As at 31 December 1951	1,514 18 6	
	Add Additions during 1952	170 4 4	
		1,685 2 10	
	Less Depreciation provided for year to date	168 10 3	
1,515			1,516 12 7
14,187			14,636 7 5
	Current Assets :—		
1,857	Stock of Publications in hand as certified by the General Secretary	6,715 10 0	
1,719	Sundry Debtors and payments in advance, including Income Tax recoverable	3,570 9 1	
—	Subscriptions in arrear (not valued)	— — —	
	Cash on Deposit with Post Office Savings Bank— £ s. d.		
1,402	General Account 1,148 19 4		
98	World Petroleum Congress 4 6 6		
		1,153 5 10	
	Cash at Bank—		
4,088	Current Account 2,028 8 3		
317	Entertainment Account 347 13 2		
		2,376 1 5	
500	Cash in hand	600 0 0	
			14,415 6 4
£24,168			£29,051 13 9

OF THE INSTITUTE OF PETROLEUM

obtained all the information and explanations which to the best of our knowledge and belief were necessary far as appears from our examination of those books. The Balance Sheet and Revenue Account are in the explanations given to us, the accounts give the information required by the Companies Act, 1948, in the 31 December 1952, and the Revenue Account gives a true and fair view of the revenue for the year ended on behalf of the Institute.

GRAHAMS, RINTOUL, HAY, BELL & CO.,
Chartered Accountants. Auditors.

THE INSTITUTE

(A Company limited by Guarantee

REVENUE ACCOUNT FOR THE

Year to 31.12.51 £		£	s.	d.	£	s.	d.
	To Administrative Expenses :—						
8,748	Staff Salaries and National Insurance .	9,071	8	0			
654	Staff Pension Scheme Contributions .	760	0	3			
9,402		9,831	8	3			
3,228	*Less* Applicable to Publications . .	3,790	1	10			
6,174		6,041	6	5			
867	Printing and Stationery . . .	836	19	0			
618	General Postages	720	9	7			
378	Telephones, Cables, and Travelling Expenses	241	14	5			
73	Audit Fee	73	10	0			
64	Legal Fees	113	17	0			
266	General Expenses	460	12	5			
27	Insurance	28	16	9			
8,467					8,517	5	7
	„ **Establishment Expenses :—**						
	Rent	2,500	0	0			
	Cleaning, Lighting, and Heating . .	440	3	7			
	Repairs and Maintenance . . .	64	2	8			
		3,004	6	3			
	Less Applicable to Publications—one-fourth	751	1	7			
2,259					2,253	4	8
	„ **Meetings :—**						
509	Hire of Hall, Pre-Prints, Reporting, etc..				594	13	11
42	„ *British National Committee—World Petroleum Conference*				—	—	—
500	„ **Sum set aside for Grants to Branches and Students' Section** . . .				500	0	0
	Grants made—						
	Northern Branch	150	0	0			
	London Branch	125	0	0			
	Trinidad Branch	68	0	0			
	Birmingham Section . . .	30	0	0			
	South Eastern Branch . . .	20	0	0			
	Persian Gulf Branch	50	0	0			
		443	0	0			
	Unallocated	57	0	0			
		500	0	0			
	„ **Sundries :—**						
	Library Expenses	246	17	11			
	Subscriptions to Societies . . .	59	14	2			
	Scholarship Awards	100	0	0			
	Depreciation of Furniture (10%) . .	168	10	3			
472					575	2	4
3,476	„ **Publications Revenue Account—Deficit for year**				5,780	10	7
1,912	„ **Balance being Surplus Revenue for Year**				80	0	6
£17,637					£18,300	17	7

OF PETROLEUM

and not having a Share Capital)

YEAR ENDED 31 DECEMBER 1952

Year to 31.12.51			£	*s.*	*d.*
£					
8,612	By	**Members' Subscriptions received for 1952** . .	9,149	5	0
188		**Members' Subscriptions in Arrear, received during year**	118	13	0
8,418	„	**Member-Company Subscriptions received for 1952**	8,566	12	6
—	„	**Member-Company Subscription in Arrear, received during year**	10	10	0
20	„	**Special Subscription**	20	0	0
399	„	**Interest and Dividends received (Gross)** . . .	435	17	1
£17,637			£18,300	17	7

PUBLICATIONS

Revenue Account for the Year ended 31 December 1952

	£	s.	d.		£	s.	d.
To Stock in hand at 1 January 1952	1,857	0	0	By Advertising	5,819	0	11
,, Dispatch Expenses	655	3	10	,, Journal	3,090	5	11
,, Journal	8,789	10	1	,, IP Review	350	12	4
,, IP Review	2,435	4	11	,, Standard Methods	3,323	9	9
,, Abstracts	485	10	6	,, Reviews of Petroleum Technology	1,602	12	0
,, Standard Methods	2,255	12	3	,, Electrical Code	227	7	0
,, Reviews of Petroleum Technology	2,203	13	6	,, Mass Spectrometry	220	7	6
,, Petroleum Measurement Manual	1,784	15	5	,, Petroleum Measurement Manual	1,131	14	6
,, Tables for Measurement of Oil	2,999	17	1	,, Tables for Measurement of Oil	822	13	0
,, Oil Shale Conference Proceedings	2,076	12	4	,, Oil Shale Conference Proceedings	694	15	0
,, Mass Spectrometry	475	10	10	,, Other Publications	914	6	10
,, Other Publications	85	19	4	,, Stock in hand at 31 December 1952	6,715	10	0
,, Publicity	16	9	1		24,912	14	9
,, Salaries, National Insurance, and Pension Scheme Contributions	3,790	1	10	,, Balance—being Deficit for year carried to Revenue Account	5,780	10	7
,, Proportion of Establishment Expenses	751	1	7				
,, Bad Debts written off	31	2	9				
	£30,693	5	4		£30,693	5	4

CADMAN MEMORIAL FUND

Income and Expenditure Account for the Year ended 31 December 1952

	£	s.	d.	£	s.	d.		£	s.	d.
To Balance at 31 December 1952 :—							By Balance at 31 December 1951	3,251	3	8
Cash at Bank on Current Account	603	1	8				,, Interest received gross	81	18	0
£2,730 3% Savings Bonds, 1965/75 (Market Value at 31 December 1952, £2,238)	2,730	0	0							
				3,333	1	8				
				£3,333	1	8		£3,333	1	8

We have examined the above Income and Expenditure Account with the books and vouchers of the Fund, and find it to be in accordance therewith. We have verified the cash at Bank and have accepted a Certificate from the Institute's Bankers for the Security held by them on behalf of the Fund.

116 Old Broad Street,
London, E.C.2.
31 *March* 1953

Grahams, Rintoul, Hay, Bell & Co.
Chartered Accountants.
Auditors.

HYDROCARBON RESEARCH GROUP

Revenue Account for the Year ended 30 September 1952

	£ s. d.	£ s. d.		£ s. d.
To **Grants :—**			By **Voluntary Contributions from Members of the Group in respect of 1952**	8,000 0 0
King's College	725 0 0			
University of Oxford	400 0 0			
University of Birmingham	1,225 0 0			
Bedford College	1,160 0 0			
Queen Mary College	1,515 0 0			
University of Liverpool	575 0 0			
University of Cambridge	950 0 0			
		6,550 0 0		
„ **Honoraria**		682 10 0		
„ **General Expenses**		9 7 3		
„ **Wages**		331 5 0		
„ **Balance being surplus for period**		426 17 9		
		£8,000 0 0		£8,000 0 0

For convenience in administration the Accounts of the Group are closed as at 30 September each year.

Statement of Funds at 30 September 1952

	£ s. d.	£ s. d.		£ s. d.
Sundry Creditor—The Institute of Petroleum		262 10 0	**Contribution due, not yet received**	1,000 0 0
Revenue Account :—			**Cash at Bank on Current Account**	662 5 9
Surplus for period	426 17 9			
Add Balance at credit at 30 September 1951	972 18 0			
		1,399 15 9		
		£1,662 5 9		£1,662 5 9

We have examined the above Revenue Account and Statement of Funds with the books and vouchers of the Group and find them to be in accordance therewith. We have verified the cash at Bank.

116 Old Broad Street,
London, E.C.2.
31 *March* 1953.

Grahams, Rintoul, Hay, Bell & Co.
Chartered Accountants.
Auditors.

CARCINOGENICITY RESEARCH FUND

Statement of Funds as at 31 December 1952

	£	s.	d.		£	s.	d.
Balance of Sum Received from the Petroleum Board (during 1947)	1,450	0	0	**Cash at Bank on Current Account**	1,450	0	0
	£1,450	0	0		£1,450	0	0

We have examined the above Statement of Funds with the books and vouchers of the Fund and find it to be in accordance therewith. We have verified the Cash at Bank.

116 Old Broad Street,
London, E.C.2.
31 *March* 1953.

Grahams, Rintoul, Hay, Bell & Co.
Chartered Accountants.
Auditors.

BENEVOLENT FUND

Income and Expenditure Account for the Year ended 31 December 1952

Year to 31.12.51		£	s.	d.	£	s.	d.	*Year to 31.12.51*		£	s.	d.
£								£				
50	To **Grant paid**				—	—	—	*2,829*	By **Balance at 31 December 1951**	2,942	11	3
	„ **Balance at 31 December 1952**				3,092	0	9	*108*	„ **Subscriptions and Donations received during year**	95	14	6
2,943	Represented by :—							*56*	„ **Interest received gross**	53	15	0
	Cash at Bank on Current Account	1,042	0	9								
	£500 3% Defence Bonds *	500	0	0								
	£1,550 2½% Defence Bonds *	1,550	0	0								
£2,993		£3,092	0	9	£3,092	0	9	*£2,993*		£3,092	0	9

* (*Market Value at 31 December 1952, £2,050.*)

We have examined the above Income and Expenditure Account with the books and vouchers of the Fund and find it to be in accordance therewith. We have verified the Cash at Bank and have accepted a Certificate from the Institute's Bankers for the Securities held by them on behalf of the Fund.

116 Old Broad Street,
London, E.C.2.
31 *March* 1953.

Grahams, Rintoul, Hay, Bell & Co.
Chartered Accountants.
Auditors.

OBITUARY

HENRY WILFRED BARNES

H. W. BARNES, B.Eng. A.M.I.C.E., was instantly killed in a motor accident on 21 August 1953. This announcement has come, and will come, as a shock to his many friends.

To all he was Bill Barnes. To his more intimate friends Bill was sufficient. It has always been so. The origin of the term Bill is obscure. The fact of its general usage would outline his pleasing and friendly character.

Born in Sheffield in 1892 Bill Barnes started his education at Sheffield Royal Grammar School. At fourteen he progressed to Ashville College, Harrogate, where at the early age of sixteen he won a scholarship to Sheffield University. In 1911 at the age of nineteen he graduated Bachelor of Engineering with first class honours. As the best student out of ninety-six he was awarded the Mappin Medal and a Government Bursary.

His first job as a draughtsman in Lewisham was a stepping stone to his position as assistant engineer and surveyor with John Mowlems. In this position he gained considerable experience in underground tunnelling on the Central London Line extension to Liverpool Street and on the Charing Cross to St. Pancras part of the Northern Line.

From John Mowlems he joined J. C. White & Co., for whom he travelled abroad to carry out civil engineering work in Para, Brazil, and Guayaquil, Ecuador. The main street in Guayaquil was part of his work. During this period he was indirectly connected with Ecuador oil. On the social side he took a keen interest in horse racing, being successful on several occasions with his own horses.

In 1922 he joined the United British Oilfields Ltd., and went out to Trinidad as fields engineer. On the conclusion of his contract with them in 1925 he joined the Lucey Oil Corp. and travelled round the world as their representative.

In 1930 he set up in London his own company, Asbestos and Engineering Products. This served to co-ordinate his various agencies in these materials. Ever interested in new engineering methods or products, welded tanks and gas holders attracted his attention. He took a sales interest in a British company pioneering this work, the Oxley Engineering Co., of which Company he eventually became a director.

Elected a Member of the Institute of Petroleum in 1923, he retained his interest in its activities. Perhaps he will be best remembered as one of that coterie of friends who met regularly in the City, and which included three Past Presidents of the Institute, Dr A. E. Dunstan, Chris Dalley, and Prof A. W. Nash.

A Founder Member of the Oil Industries Club, he took an active part in its formation and in its development.

Typically John Bull in appearance, he attacked everything with zest,

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He was buried in Shirley Parish Churchyard on 28 August.

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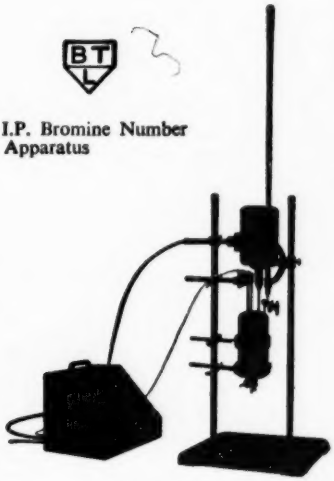

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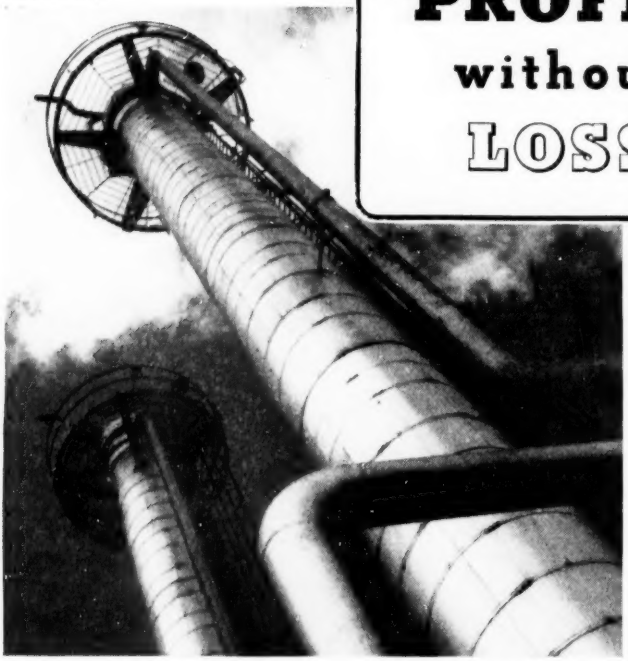

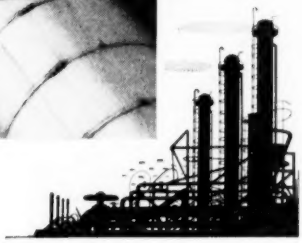

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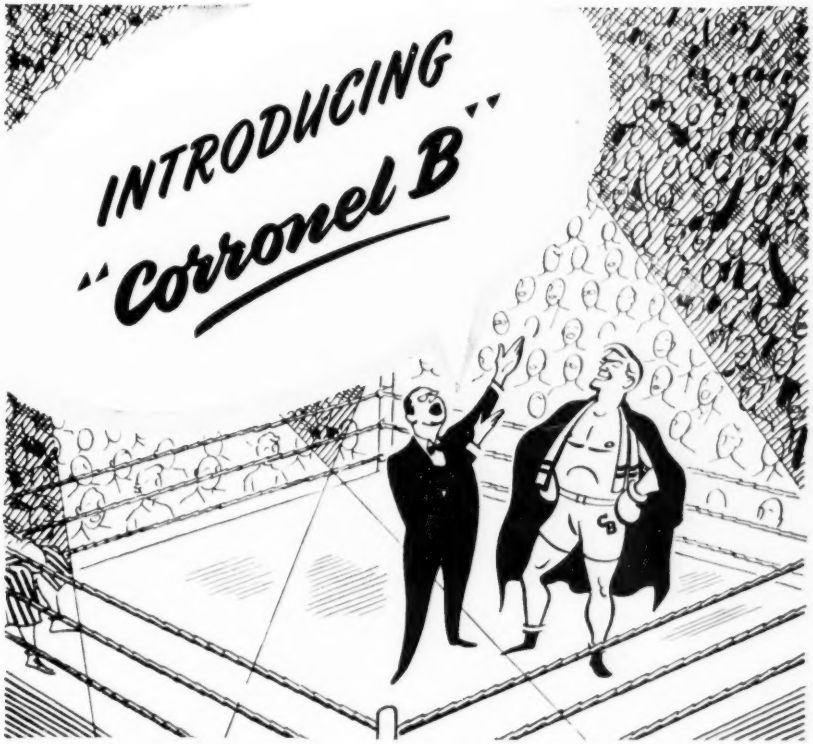

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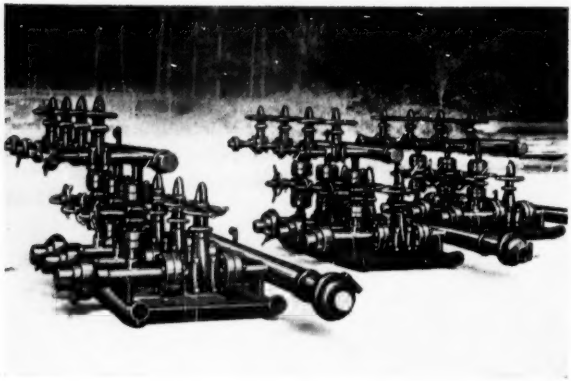

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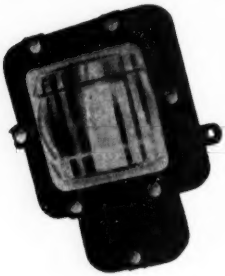

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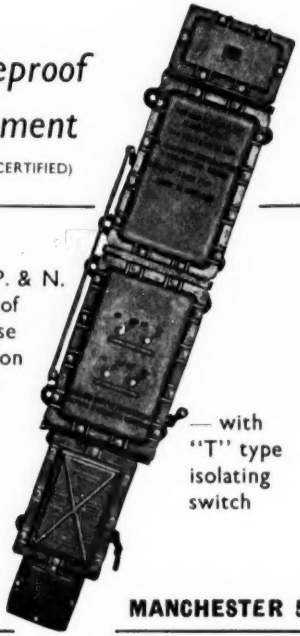

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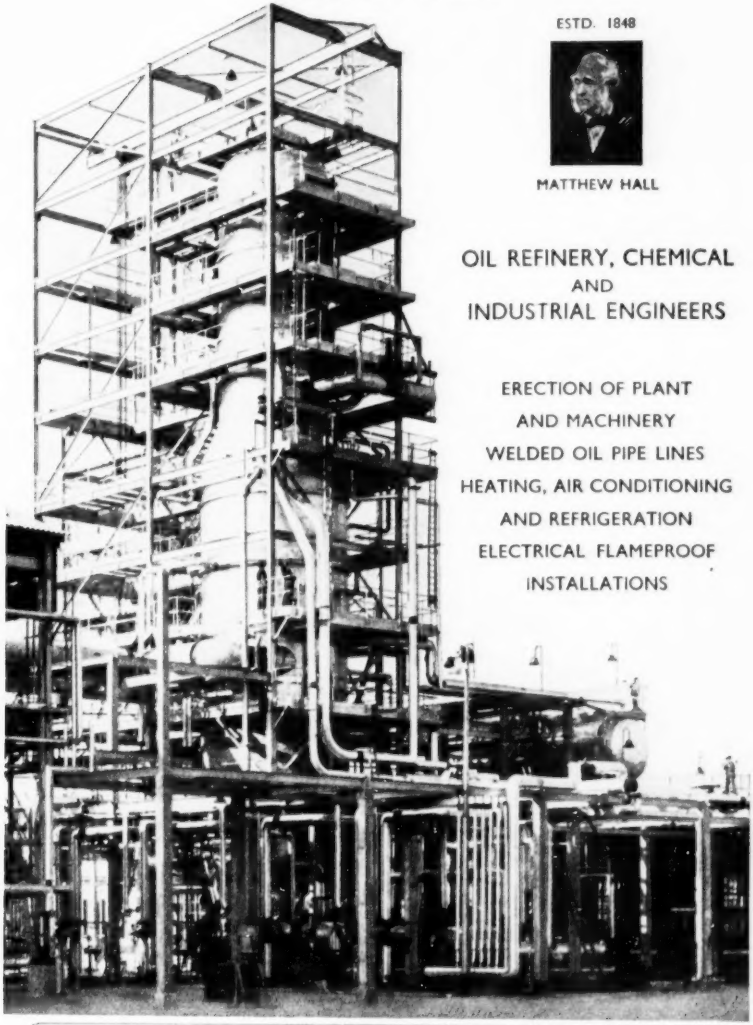

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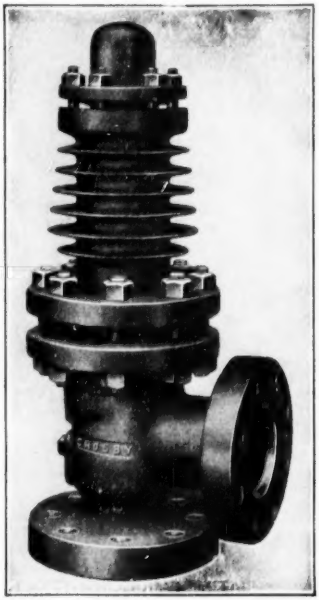

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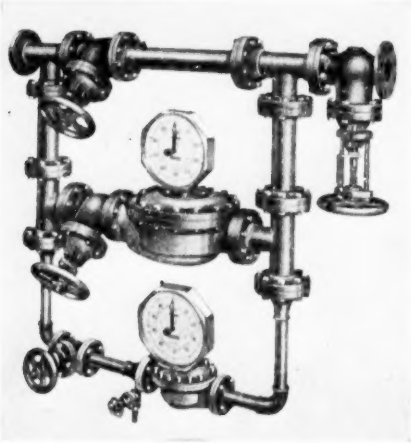

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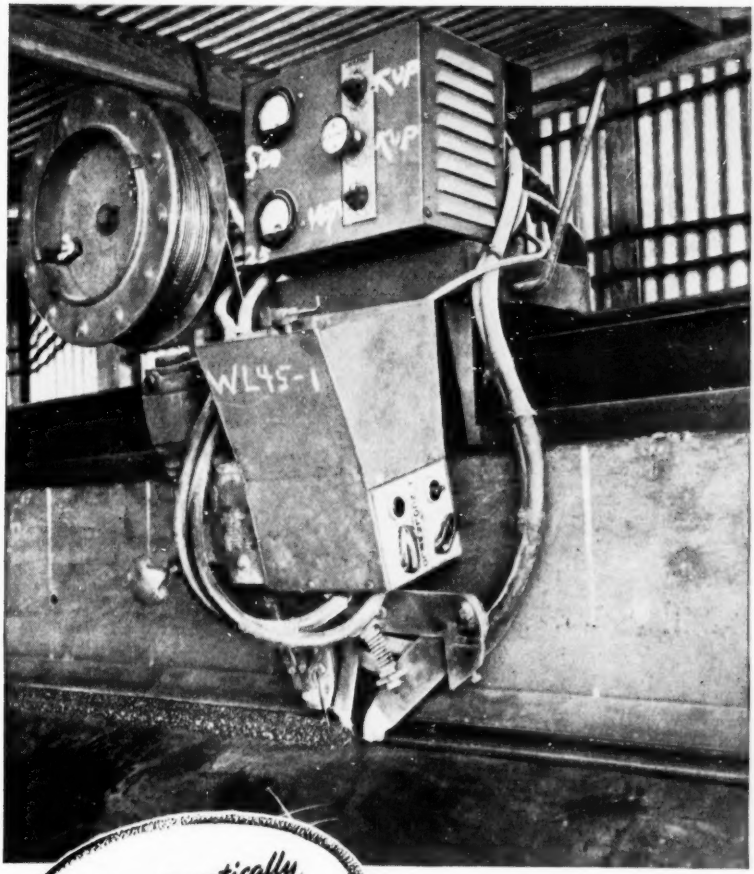

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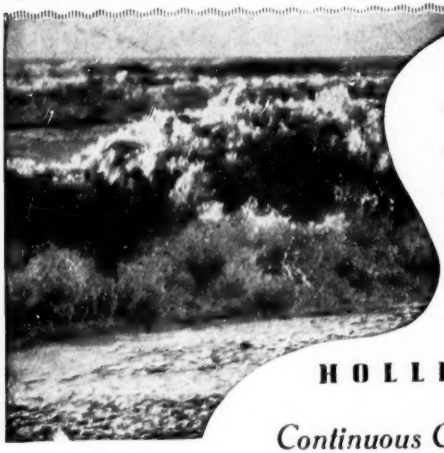

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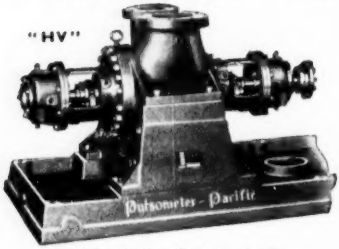

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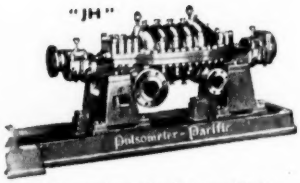

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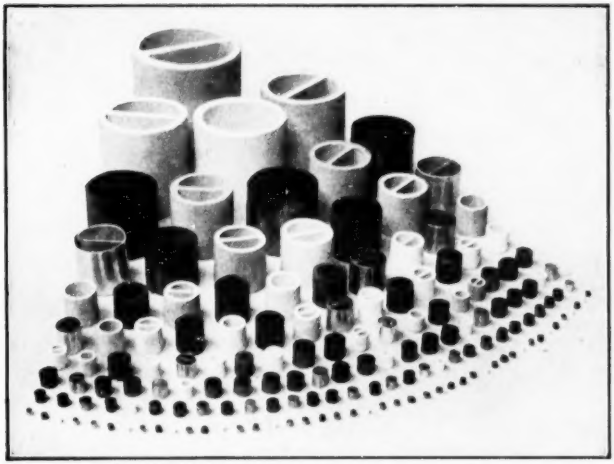

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